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Fourier Transform Infrared Spectrometry of Ambient Aerosols

Lawrence Berkeley Lab., CA

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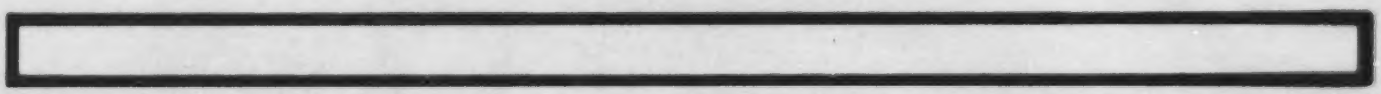

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Fourier transform infrared (FTIR) spectrometry has been evaluated as a method for determining the concenration of selected species present in ambient aerosols collected on Teflon filters. The filters are analyzed by transmission measurements after collection of the fine fraction (<2.5 μm diameter) of the ambient particles on 2 μm pore size Teflon filters. The spectra of the blank filters are subtracted from the spectra of the loaded filters and the area of the specific absorbance bands for ammonium, nitrate, and sulfate are measured and compared to calibration curves. The filter orientation must be maintained for all measured infrared spectra.

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FOURIER TRANSFORM INFRARED SPECTROMETRY OF AMBIENT AEROSOLS

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ABSTRACT

Fourier transform infrared (FTIR) spectrometry has been evaluated as a method for determining the concentration of selected species present in ambient aerosols collected on Teflon* filters. The filters are analyzed by transmission measurements after collection of the fine fraction (< 2.5 μm diameter) of the ambient particles on 2 μm pore size Teflon* filters. The spectra of the blank filters are subtracted from the spectra of the loaded filters and the area of the specific absorbance bands for ammonium, nitrate, and sulfate are measured and compared to calibration curves. The filter orientation must be maintained for all measured infrared spectra.

Calibration curves were developed for sulfate and ammonium nitrate from measurements of laboratory generated particles. The lower limit of detection (LLD) for laboratory generated sulfate, calculated from measurements of the 620 cm^{-1} absorption band, is 1.7 $\mu g/cm^2$ (3σ). The LLD for the sulfate band at 1117 cm^{-1} is 0.2 $\mu g/cm^2$, however this band cannot be used in the analysis of ambient aerosol samples because of spectral interferences. The LLD for laboratory generated ammonium nitrate is 1.32 $\mu g/cm^2$. Multicomponent analysis methods were developed to analyze ammonium nitrate in the presence of ammonium sulfate.

Ambient aerosols were collected during the Carbonaceous Methods Species Methods Intercomparison (CARB) study. The filters were analyzed for sulfate by both FTIR and Ion Chromatography (IC). There is good agreement between sulfate analysis by IC and analysis of the FTIR transmission spectra of the air filters. The LLD for ambient sulfate was measured to be 5.8 $\mu g/cm^2$. If filter orientation is maintained the LLD is estimated to be 1 - 2 $\mu g/cm^2$.

The CARB study samples were also analyzed for elemental carbon using FTIR. Intercomparisons were made with results obtained from the analysis of co-collected quartz filter samples using a thermal combustion method of analysis. Good correlation was found between the infrared absorbance in the 650 - 666 cm^{-1} region of particles collected on Teflon* filters and the elemental carbon determined from analysis of the quartz filters. Attempts to develop a direct elemental carbon calibration standard on Teflon* filters were unsuccessful. It was concluded that calibrations must be made with co-collected air samples on quartz filters analyzed by thermal methods.

The chemical interactions on the filter between ammonium nitrate and ammonium sulfate were studied. It was determined that both compounds can interact to form the nonvolatile mixed salts $2NH_4NO_3.(NH_4)_2SO_4$ and $3NH_4NO_3.(NH_4)_2SO_4$. NH_4NO_3 was found to react on the filter with NaCl to form $NaNO_3$ and volatile NH_4Cl. A procedure based on this reaction is proposed as a method to retain nitrate ion on Teflon* filters.

In order to analyze large numbers of filter samples, the FTIR spectrometer was modified by the addition of an automatic sample changer. The sample changer compartment accepts the filter carousel from a Sierra/ Anderson model 245* automated dichotomous sampler. The motion of the sample changer is completely controlled by the FTIR computer.

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SECTION 1

INTRODUCTION

The collection and analysis of ambient aerosols is an important means of studying the chemistry of the troposphere. The major constituents of the fine fraction (< 2.5 μm diameter) of the particulate matter in the atmosphere are ammonium sulfate, ammonium nitrate, and elemental and organic carbonaceous particles. Knowledge of the origins, interaction, and deposition of these compounds is important in the study of visibility degradation, atmospheric chemistry, acid deposition, and the effects of these particles on human health and terrestrial ecology.

Ambient aerosols are typically collected with dichotomous air samplers (Loo, 1979) which collect particles in two size fractions. The fine fraction particles are < 2.5 μm in diameter and the coarse fraction particles are in the 2.5 - 15 μm diameter size range. The size fractions correspond to the bimodal distribution of particles sizes found in the atmosphere. The particles are collected on various filter media including Teflon*, Nylon, quartz, and paper filters. The choice of filter media depends, among other things, upon the compounds to be measured, on the analysis technique to be used, and the cost of the filters.

There are a number of chemical analysis techniques available to measure the concentrations of elements and compounds collected on air filters. Sulfate and nitrate ions collected on the filters are typically measured using ion chromatography. Ion chromatography is a very sensitive but destructive analytical technique for the determination of sulfate, nitrate, and a number of other ions (Mulik, et al., 1976). The method requires liquid extraction, followed by separate analysis of cation and anions, and provides no direct information concerning compound speciation of the ions. In addition, the extraction procedure can alter the species found on the filter.

Another method for determining sulfate collected on filters is x-ray fluorescence (XRF) analysis. This nondestructive method of analysis has been used in an automated system to determine elemental sulfur, as well as other elements, deposited on Teflon* filters (Jaklevic, 1976). Sulfate concentrations can be inferred by assuming that all of the sulfur is in the form of sulfate. Ion chromatography analysis for sulfate has been compared to XRF analysis for sulfur on Teflon* air filters and the two methods have been shown to provide equivalent results for sulfate (Stevens, 1978). X-ray fluorescence provides no information concerning nitrate deposition due to the low energy of the characteristic nitrogen x-ray emission.

X-ray diffraction is a nondestructive technique that can provide for compound identification. It is difficult to obtain quantitative results using x-ray diffraction for two reasons: 1) The sensitivity of this technique is relatively low. Consequently, high particle loadings are required to obtain adequate measurements for accurate compound identification. High particle loadings introduce the possibility of chemical reactions between particles concentrated on the filter. 2) Water in the sampled air can promote recrystallization of particles on the filter. This introduces a preferred orientation in the sample which will change the peak ratios in the diffraction signals causing difficulties in calibration.

Recently, another method for particle analysis on Teflon* filters has been reported. McClenny, et al. (1985) have shown that ammonium and sulfate can be measured directly on Teflon* filters using Fourier transform infrared (FTIR) transmission spectrometry. Their results showed the equivalence of XRF and FTIR spectroscopy for the quantitative determination of sulfate. They also reported quantitative measurements of the ammonium cation. In addition to the discrete absorption bands associated with the vibrational modes of specific molecular species, the mid-infrared spectrum of these ambient aerosols shows continuous absorption across the entire spectrum which is characteristic of carbonaceous particles. To the extent that a relationship between this absorption and the elemental carbon content can be established, a method for nondestructive automated analysis of carbon particle concentration simultaneously with that for sulfate, ammonium, and

nitrate particles could result. Finally, this technique is appealing because it makes use of a common filter media, Teflon*, is nondestructive, requires no sample preparation, is amenable to automation, and can provide simultaneous analysis of compounds that typically require different types of analysis on different filter media.

This report describes an experimental program intended to build on the initial work of McClenny, et al. (1985). A number of suggestions were proposed in that paper to improve lower limits of detection for sulfate. These have been implemented and tested. Experiments to test analytical methods to quantitatively determine sulfate, nitrate, ammonium, and elemental carbon on laboratory generated samples and ambient samples will be described.

A Fourier transform infrared (FTIR) spectrometer was modified with the addition of an automatic sample changing compartment. The FTIR instrument and sample changing compartment will be described; however, a detailed description of the FTIR system can be found in the operating manual accompanying the instrument.

SECTION 2

CONCLUSIONS

Automated FTIR analysis of aerosol samples using a Nicolet model 5DXB* Fourier transform infrared spectrometer has been realized with the design and construction of a specialized sample handling system. The sample compartment directly accepts the sample carousel from a commercial air sampler produced by Sierra/Andersen Inc.* thereby minimizing sample handling. Software was developed and added to the existing data collection and analysis programs in the Nicolet* FTIR to allow complete control of the position of any filter. Software was also written to analyze ambient air samples by automatically providing an optimal background subtraction and integration of absorption bands of interest of the collected particles. This instrument provides automated nondestructive sulfate analysis of up to 40 Teflon* air filters with minimal sample handling and operator intervention.

Quantitative spectral analysis methods were developed to analyze sulfate in aerosols collected on Teflon* filters. Laboratory experiments showed that detection limits are eight times lower for analysis using the sulfate absorption band at 1117 cm^{-1} than for the band at 620 cm^{-1}. However, spectral interferences found in ambient samples prevented use of this former band for routine sulfate analysis. Analysis of air samples collected in Los Angeles during the California Air Resources Board Carbonaceous Species Methods Comparison (CARB) Study showed good correlation of the FTIR method of analysis for sulfate with ion chromatography (IC) analysis of the same sample filters.

Small improvements in the detection limit for sulfate using the 620 cm^{-1} band were realized by using 2 μm pore size Teflon* filters, saving reference spectra of each blank filter prior to air sampling for use during background subtraction, and maintaining the physical orientation of

the filters during infrared spectral measurements. All of these practices contribute to more accurate background subtraction which leads to a more accurate measurement for sulfate. The lower limit of detection for sulfate in ambient aerosols using the 620 cm^{-1} absorption band was measured to be 5.8 $\mu g/cm^2$ during the CARB study in which the filter orientation was not maintained throughout the analysis. If filter orientation is maintained then the lower limit of detection is estimated to be 1 - 2 $\mu g/cm^2$ for ambient sulfate.

Spectral analysis methods were developed to quantitatively measure ammonium nitrate in the presence of interferences due to ammonium sulfate. Ammonium nitrate measurements were accurate to within 3 - 5% after ammonium sulfate spectral interferences were removed on laboratory prepared aerosol samples. The lower limit of detection for the measurement of ammonium nitrate was found to be 1.32 $\mu g/cm^2$ for laboratory generated samples.

A high degree of correlation was found between elemental carbon measurements on infrared spectra of ambient samples collected on Teflon* filters and elemental carbon measured by thermal methods on samples collected on quartz filters. However, attempts to develop a direct elemental carbon calibration standard on Teflon* filters using laboratory generated soot particles was unsuccessful. It was concluded that calibrations must be made with co-collected air samples on quartz filters analyzed by thermal methods.

The sensitivity of infrared analysis to specific compounds represents a unique advantage for performing quantitative chemical measurements of ambient aerosols. The 2:1 and 3:1 mixed salts of ammonium nitrate and ammonium sulfate were identified on ambient filters collected during the CARB study. The Fourier transform infrared spectrometer also provides an ideal means for studying the dynamics of chemical reactions occurring on the filter. Laboratory experiments showed that nitrate ion could be trapped on the filter by reactions of ammonium nitrate with NaCl but experiments with ambient samples were unsuccessful.

SECTION 3

RECOMMENDATIONS

It is recommended that this technique and instrument be incorporated into an air sampling and analysis network in order to develop an intercomparison database to further evaluate this instrument relative to other methods of analysis. This instrument can easily be incorporated into an existing air sampling network because it uses a common filter medium, Teflon*, performs nondestructive analysis, and is designed to handle large numbers of samples in an automated system. Additional ambient samples are required to:

1. Determine the collection parameters such as, sampling time and flow rates, to provide adequate samples for analysis within the constraints of the sensitivity of the analytical method.
2. Determine the type of spectral interferences that will occur in various sampling environments.
3. Confirm the correlation for sulfate measured by Fourier transform infrared analysis and ion chromatography.
4. Collect carbon samples on quartz filters in parallel with Teflon* filter samples to develop a calibration for elemental carbon.
5. Collect a sufficient number of samples containing ammonium nitrate and carbon to develop an empirical method to determine the baseline underneath the ammonium nitrate absorption band.

SECTION 4

GENERAL EXPERIMENTAL PROCEDURES

MODIFIED FOURIER TRANSFORM INFRARED SPECTROMETER

The Fourier transform infrared (FTIR) spectrometer is a Nicolet model 5DXB* capable of 2 wavenumber (cm^{-1}) resolution. A flipper mirror option has been installed to direct the infrared beam out of the main optical bench and into an automatic sample changer compartment. The deuterated triglycine sulfate (DTGS) detector has been been removed from the main FTIR optical bench and mounted in the sample changer compartment. An associated computer is equipped with a 36 megabyte hard disk, a 1 megabyte floppy disk, and 640 kilobytes of extra direct memory access to provide adequate programming and file storage space. Figure 4-1 is photograph of the entire instrument including the sample changer compartment.

The sample changer compartment is shown in detail in Figure 4-2. The compartment has been designed to directly accept the sample carousel from a Sierra/Andersen model 245* automated dichotomous sampler. The Teflon* filters are 37 mm, 2 μm pore size Teflon* filters. They are placed in circular filter holders which are in turn placed in the circular sample carousel. The carousel holds 20 pairs of filters in the coarse and fine fraction channels of the dichotomous air sampler. The flipper mirror in the main FTIR optical bench directs the infrared beam into the sample changer compartment. Additional sample focusing mirrors are mounted in the sample changer compartment to direct the infrared beam downward through the Teflon* filters and into the DTGS detector mounted below the carousel. The infrared beam covers an approximately 15 mm diameter area on the Teflon* filter thus averaging over any nonuniformity in particle deposition. The DTGS detector can be replaced with a mercury cadmium telluride detector (MCT). The MCT

detector is more sensitive than the DTGS detector but it does not have the wide linear dynamic range of a DTGS detector.

A computer-controlled stepper motor rotates the carousel in a clockwise direction to position the filters for analysis. Another stepper motor moves the carousel horizontally to select either the inner or outer concentric circle of filters. Software was written to allow the FTIR computer to communicate to a microcomputer (BASICON model 2N*, Portland, OR) mounted in the sample changer compartment. This microcomputer controls and monitors the carousel stepper motors and microswitches. Data collection, data storage, and the positioning of the correct filter in the infrared beam can all be controlled from the Nicolet 1280* computer. Each filter can be measured and analyzed in 4 - 5 minutes.

AEROSOL GENERATOR

An existing laboratory aerosol generator was used to generate particulate samples of ammonium sulfate, ammonium nitrate and other compounds for laboratory experiments. The particles were generated using a constant output collision nebulizer (TSI model 3075*) (May, 1973). The compound in solution is aspirated into the nebulizer. The aerosol from the nebulizer is dried with a silica diffusion dryer and is charged-neutralized in a Kr-85 diffusion discharger. The particles are deposited on the filter using the fine particle (< 2.5 μm diameter) channel of a dichotomous air sampler. The solutions were prepared by mixing 2 mg/mL of the reagent grade compound, such as ammonium sulfate or ammonium nitrate, with water. The laboratory-generated particles produce an infrared absorption spectrum that is identical to that seen in ambient samples. Scanning electron micrographs show that the laboratory-generated ammonium sulfate particles are on the order of 1 - 2 μm in size while ambient particles are in the 0.1 - 1 μm range. There does not appear to be any detectable difference in infrared absorption of particles in these two size distributions. The particles from the generator can also be mixed with humid air to provide an aerosol sample of almost any desired relative humidity.

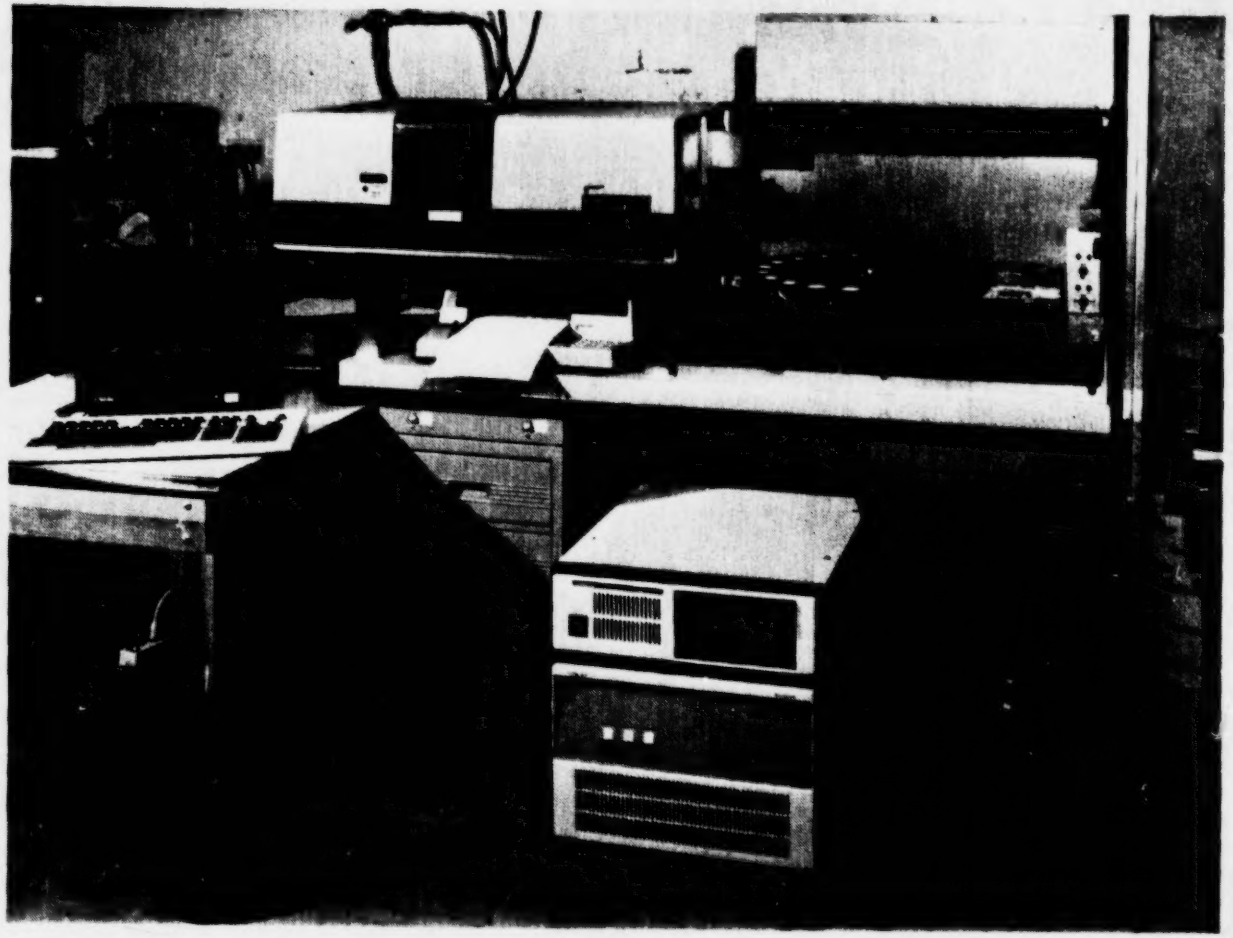

Fig. 4-1. Fourier transform infrared spectrometer and sample changer compartment.

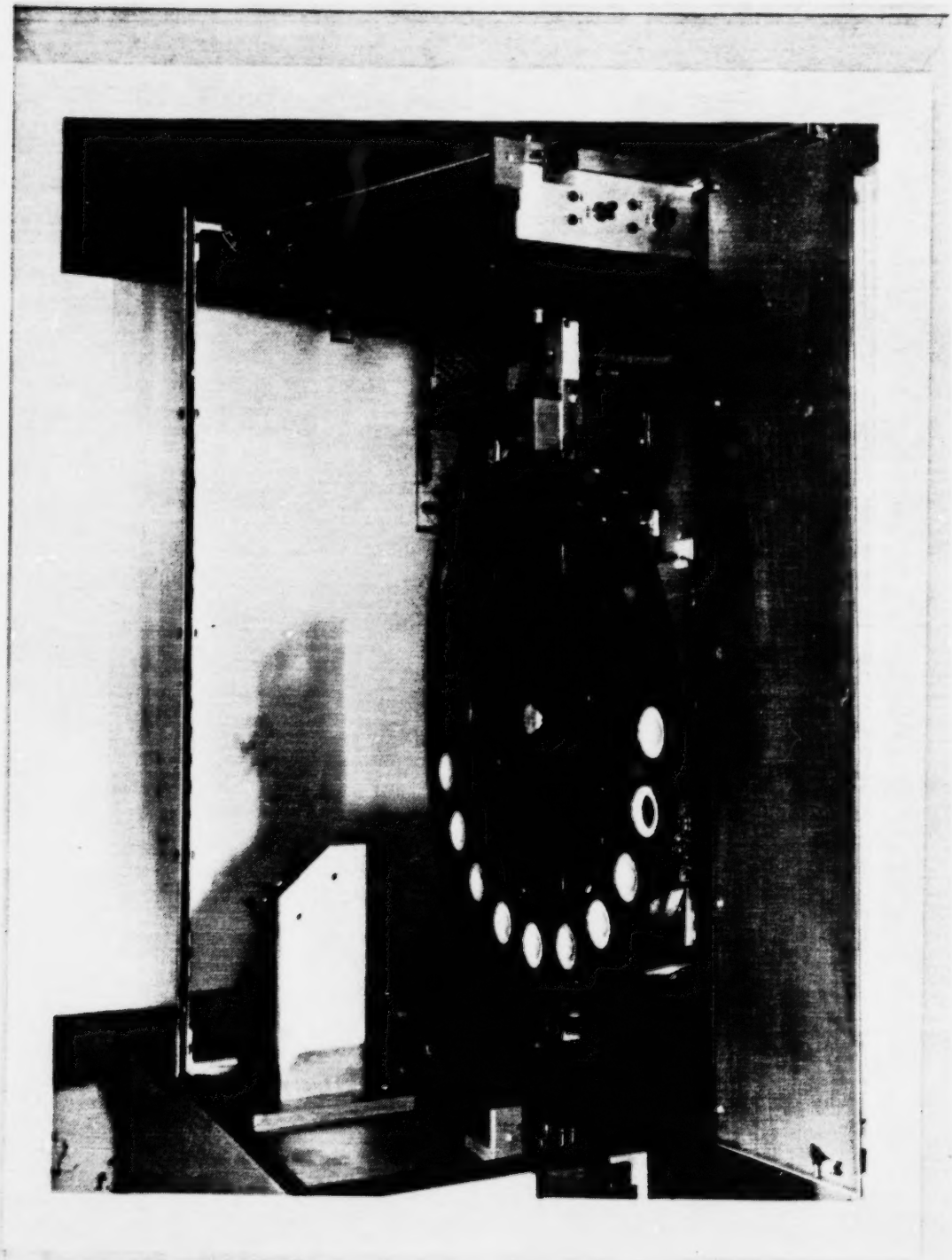

Fig. 4-2. Sample changer compartment.

CALIBRATION STANDARDS

Ammonium sulfate calibration standards were prepared by depositing laboratory-generated ammonium sulfate on Teflon* filters and then analyzing the filters for total sulfur using x-ray fluorescence. These standards were used to calibrate the instrument for the determination of sulfate particle concentration on ambient filter samples. The sulfate concentration on the 25 calibration filters ranged from 5 - 67 $\mu g/cm^2$ as determined from the total sulfur measurements by x-ray fluorescence. The infrared spectra of the standard filters were measured before and after particle deposition. Each infrared spectra was integrated at 100 scans, 2 cm^{-1} resolution. The sample compartment was purged with dry air. The filter orientation was maintained throughout the analysis. Figure 4-3 is an infrared spectrum of laboratory-generated ammonium sulfate. Sulfate absorption occurs at 1117 cm^{-1} and 620 cm^{-1}. Ammonium absorption occurs at 1424 cm^{-1}. The calibration equation for the 620 cm^{-1} absorption band in the 595 - 635 cm^{-1} region is: SO_4 ($\mu g/cm^2$) = 22.223 * (SO_4 area) - 0.443 (N = 25, r = 0.996). The 3σ lower limit of detection based on this calibration is 1.7 $\mu g/cm^2$.

Ammonium nitrate calibration standards were prepared by depositing laboratory-generated ammonium nitrate on Teflon* filters and then analyzing the filters for nitrate using both FTIR and ion chromatography. A 100 µl drop of ethyl alcohol was deposited on the particle side of each filter to promote wetting. The filters were then placed, particle side down, in 10 mL of water. Next, the filters were extracted in a sonic bath for 30 minutes. The filters were analyzed the same day they were prepared to minimize any possible loss of mass due to volatilization at room temperature. The Teflon* filter spectra were measured before and after particle deposition. The standards were used to determine ammonium nitrate particle concentration on ambient filter samples. The ammonium nitrate concentration on the 14 calibration filters ranged from 5 - 29 $\mu g/cm^2$. The infrared spectra were measured for each filter before and after particle deposition. Each infrared spectrum was taken at 100 scans, 2 cm^{-1} resolution, and the filter orientation was maintained throughout the analysis. The sample compartment was purged with dry air. Figure 4-4 is an infrared spectrum of laboratory-generated ammonium nitrate. Nitrate absorption occurs at 1371 cm^{-1} and 832 cm^{-1}.

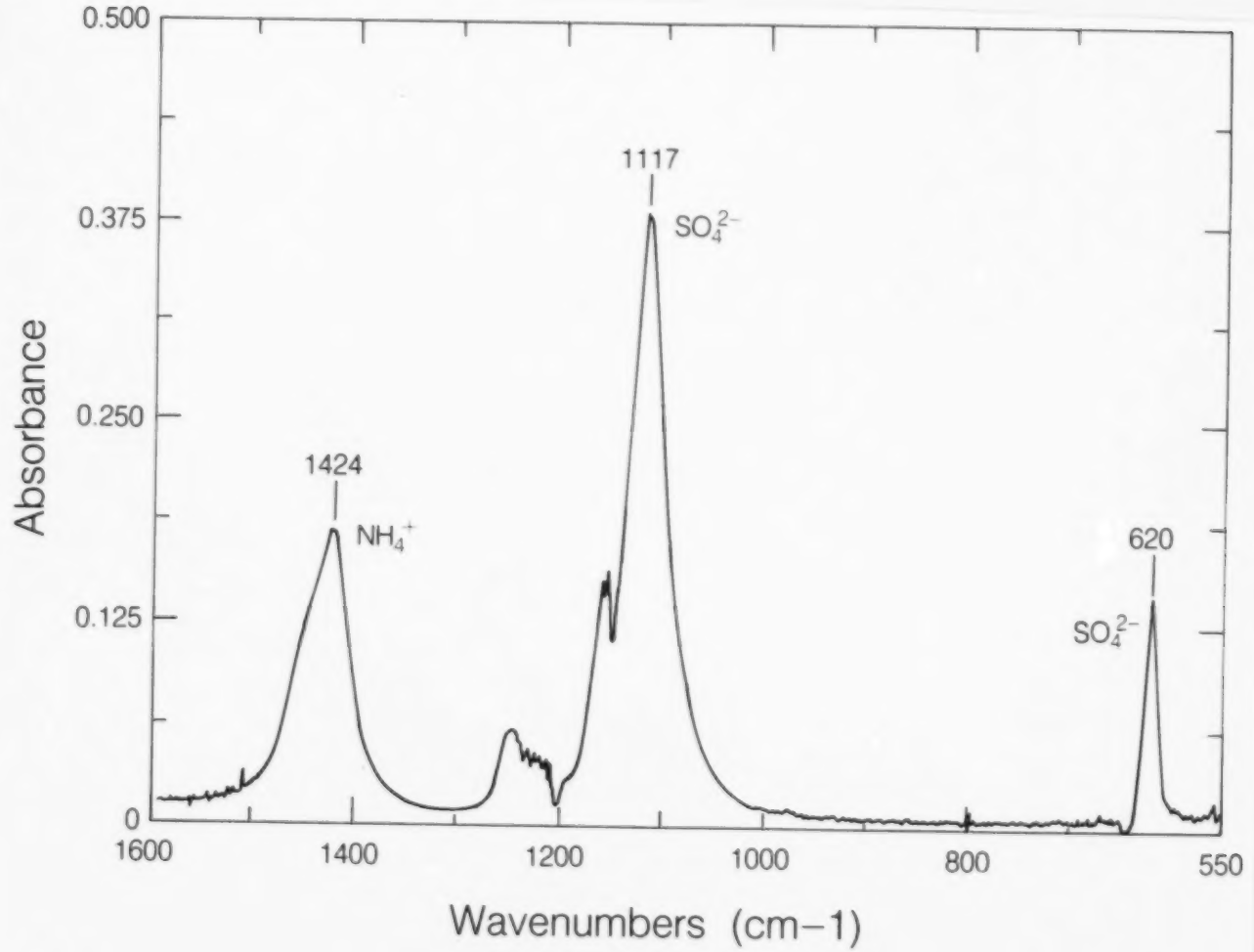

Fig. 4-3. Ammonium sulfate spectrum.

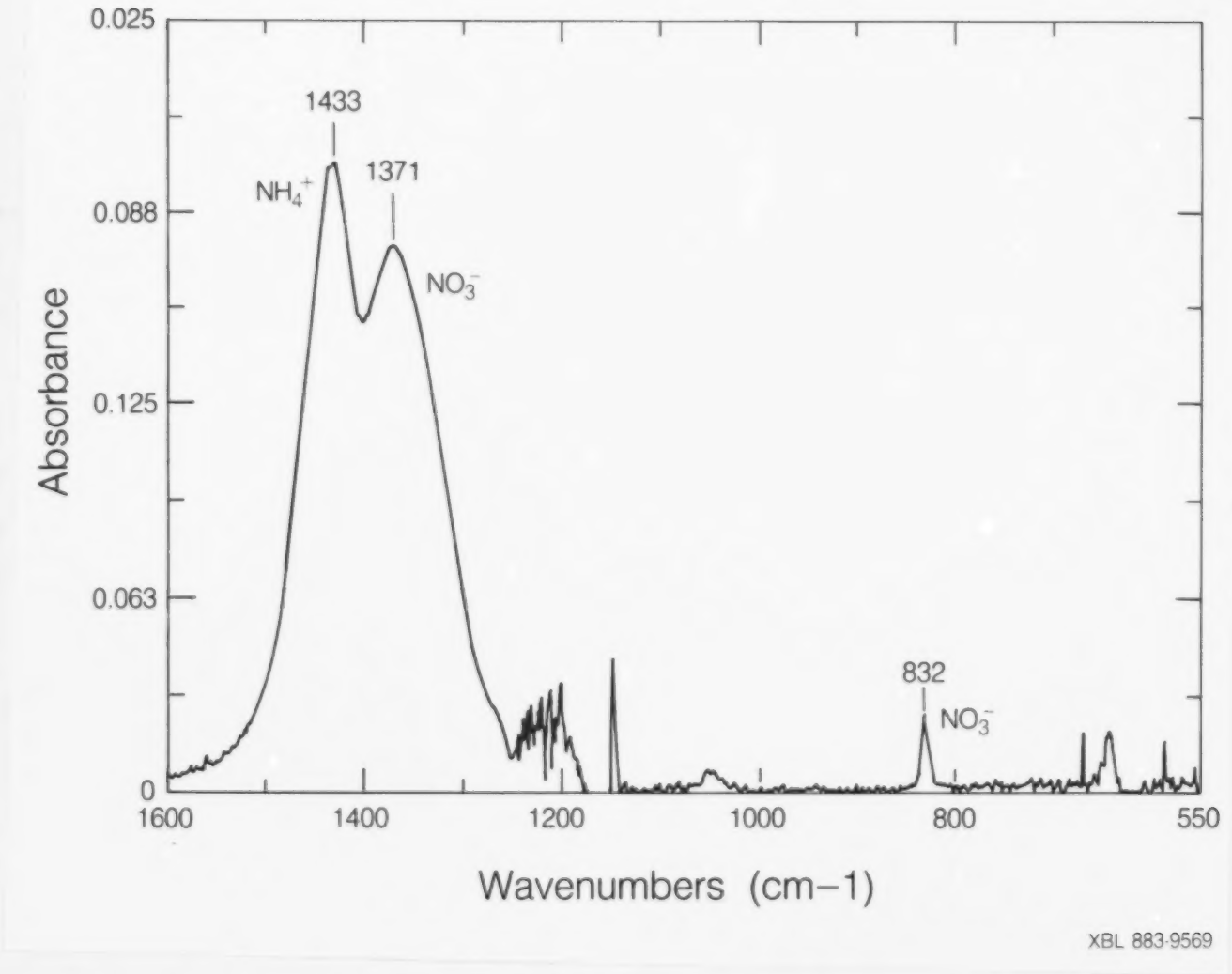

Fig. 4-4. Ammonium nitrate spectrum.

Ammonium absorption occurs at 1433 cm^{-1}. The area of the combined ammonium and nitrate bands were measured by integrating the absorbance in the 1320 - 1530 cm^{-1} region of the spectrum. The calibration equation is: NH_4NO_3 ($\mu g/cm^2$) = 1.069 * (NH_4NO_3 area) - 1.262 (N = 14, r = 0.998). The 3σ lower limit of detection based on this calibration is 1.32 $\mu g/cm^2$.

SECTION 5

ANALYSIS OF LABORATORY-GENERATED AMMONIUM SULFATE

INTRODUCTION

Analysis of the infrared spectra used to determine sulfate concentration requires that the overlapping absorption bands of the Teflon* substrate be subtracted from the sulfate bands at 620 cm^{-1} and 1117 cm^{-1}. Correction for the Teflon* substrate background is achieved by subtracting the spectrum obtained from a blank filter from the spectrum of the same filter after particle deposition. The residual absorption spectrum is due only to the collected particles and not due to absorption of the Teflon* filter. McClenny, et al. (1985) reported difficulty in completely subtracting the strong Teflon* bands in the 1000 - 1300 cm^{-1} region of the 1 μm filters. In practice, the results of spectral subtraction procedures are extremely sensitive to any differences, such as absorbance band shape and band positions, between the two spectra (Hirschfeld, 1975a, 1975b, 1976). This problem is especially severe for absorption bands with a maximum absorbance greater than one. Figure 5-1 shows the difference between the infrared absorbance spectra of a 1 μm pore size and a 2 μm pore size Teflon* filter. Accurate background subtraction is impossible for the totally absorbing bands in the 1000 - 1300 cm^{-1} region of the 1 μm pore size filter. Good background subtraction results should be possible with the 2 μm filters as long as the maximum absorbance is less than one absorbance unit.

SPECTRAL SUBTRACTION PROCEDURES

The following strategy for the analysis of sulfate was implemented following suggestions proposed by McClenny, et al. (1985).

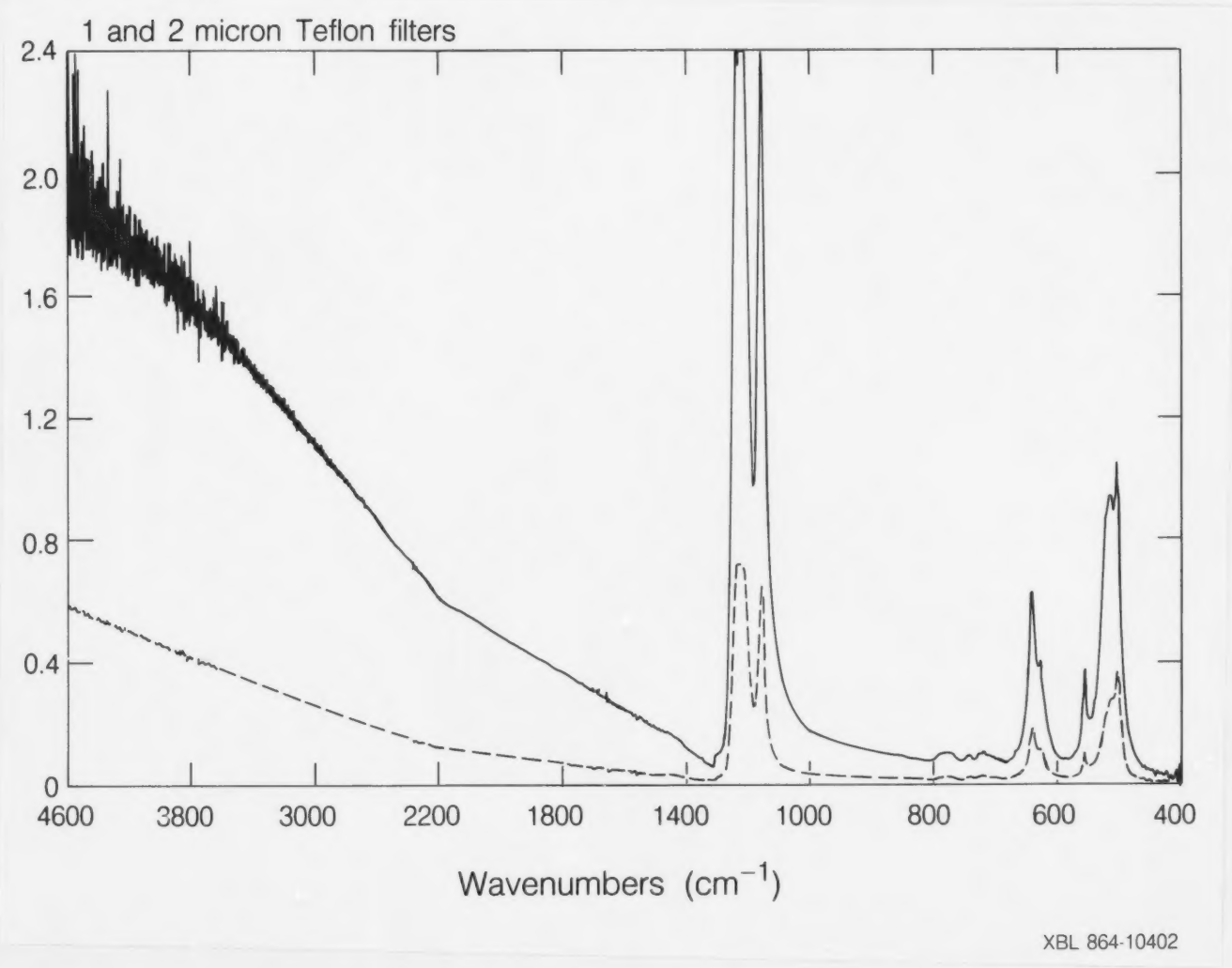

Fig. 5-1. Blank 1 μm (solid line) and 2 μm (dashed line) pore size Teflon* filter spectra.

1. Two micron pore size Teflon* filters were used throughout the analysis.
2. Infrared spectra of each blank filter was measured and stored as absorbance data files prior to deposition of the ammonium sulfate.
3. Spectral subtraction for a particulate sample is always performed by subtracting the spectrum of the same blank filter acquired before particle deposition.

This strategy should ensure that the maximum filter absorbance is always low enough to provide an accurate subtraction and that the blank and loaded filter spectra are identically matched. In practice, the subtraction of a blank filter from a loaded filter is not a simple one-to-one subtraction process. Subtraction is performed, on the Nicolet 5DXB* FTIR, according to the following formula:

RESULT SPECTRUM = SAMPLE SPECTRUM - FCR*REFERENCE SPECTRUM

where the variable FCR is a scale factor approximately equal to one. The value of FCR is varied until the background subtraction is judged to be complete by some specifically defined criterion. Background subtraction was judged to be complete when the integrated area in the region 1135 - 1300 cm^{-1} was zero. This criterion is based on the assumption that a horizontal background spectrum of zero absorbance should result after completely subtracting the Teflon* substrate absorbance spectrum.

A set of ammonium sulfate calibration standards were prepared as described in Section 4 however, no attempt was made to maintain filter orientation at this time. The absorbance band regions that were measured were 1300 - 1550 cm^{-1} for ammonium, 1000 - 1135 cm^{-1} for sulfate, and 596 - 640 cm^{-1} for sulfate.

RESULTS

The vibrational absorbance bands of importance for sulfate (Figure 4-3) are from 596 - 640 cm^{-1} with a peak absorbance at 620 cm^{-1} and from 1000 - 1200 cm^{-1} with a peak absorbance at 1117 cm^{-1}. The ammonium band of importance is from 1300 - 1550 cm^{-1} with a peak absorbance at 1420 cm^{-1}. Another

strong ammonium band in the 2400 - 3520 cm^{-1} region was not used because it lies in an area of significant scattering of the infrared light by the filter and because of the lower signal-to-noise ratio due to decreased lamp intensity in this energy region. The ammonium band at 1420 cm^{-1} does not overlap any other band but it does lie in a region of significant water absorption which would indicate that the instrument should be purged of water vapor to achieve maximum noise reduction for this band. Although both sulfate bands overlap Teflon* bands found in the regions 1000 - 1300 cm^{-1} and 600 - 675 cm^{-1}, the background subtraction protocol successfully corrects for this interference.

Figure 5-2 is a graph of the mass loading (in $\mu g/cm^2$ as determined by XRF) versus the integrated areas of the ammonium and sulfate bands after background subtraction of the blank filter spectra. The filter orientation was not maintained for the set of calibration standards shown in Fig. 5-2. A linear least squares line was fit to each set of data and a clear linear relationship can be seen. The error in the slope and intercept for each line was calculated and a lower limit of detection (LLD = 3σ) was determined using a propagation of errors approach (Long, 1983). Table 1 shows the calculated lower limits of detection for ammonium and sulfate on 37 mm, 2 μm Teflon* filters for each absorption band. The last column shows the equivalent ammonium sulfate particulate concentration in air corresponding to a 24 hr sampling period with a typical dichotomous sampler operating a flow rate of 0.9 m^3 per hour.

The experiments on laboratory-generated ammonium sulfate were designed to determine if improvements could be made in the lower limit of detection (LLD) for sulfate and ammonium. McClenny, et al. (1985) reported LLDs of 0.35 and 4.0 $\mu g/cm^2$ for sulfate (620 cm^{-1} absorption band) based on two independent calculations. Similar calculations for ammonium produced LLDs of 0.53 and 1.5 $\mu g/cm^2$. Our measured LLD for ammonium, shown in Table 1, is better than that reported by McClenny, et al. (1985). Our measurements for sulfate (620 cm^{-1}) are similar to those reported by McClenny, et al. (1985). The more strongly absorbing sulfate band at 1117 cm^{-1} has been found to be eight times more sensitive than the weaker sulfate absorption band at 620 cm^{-1}.

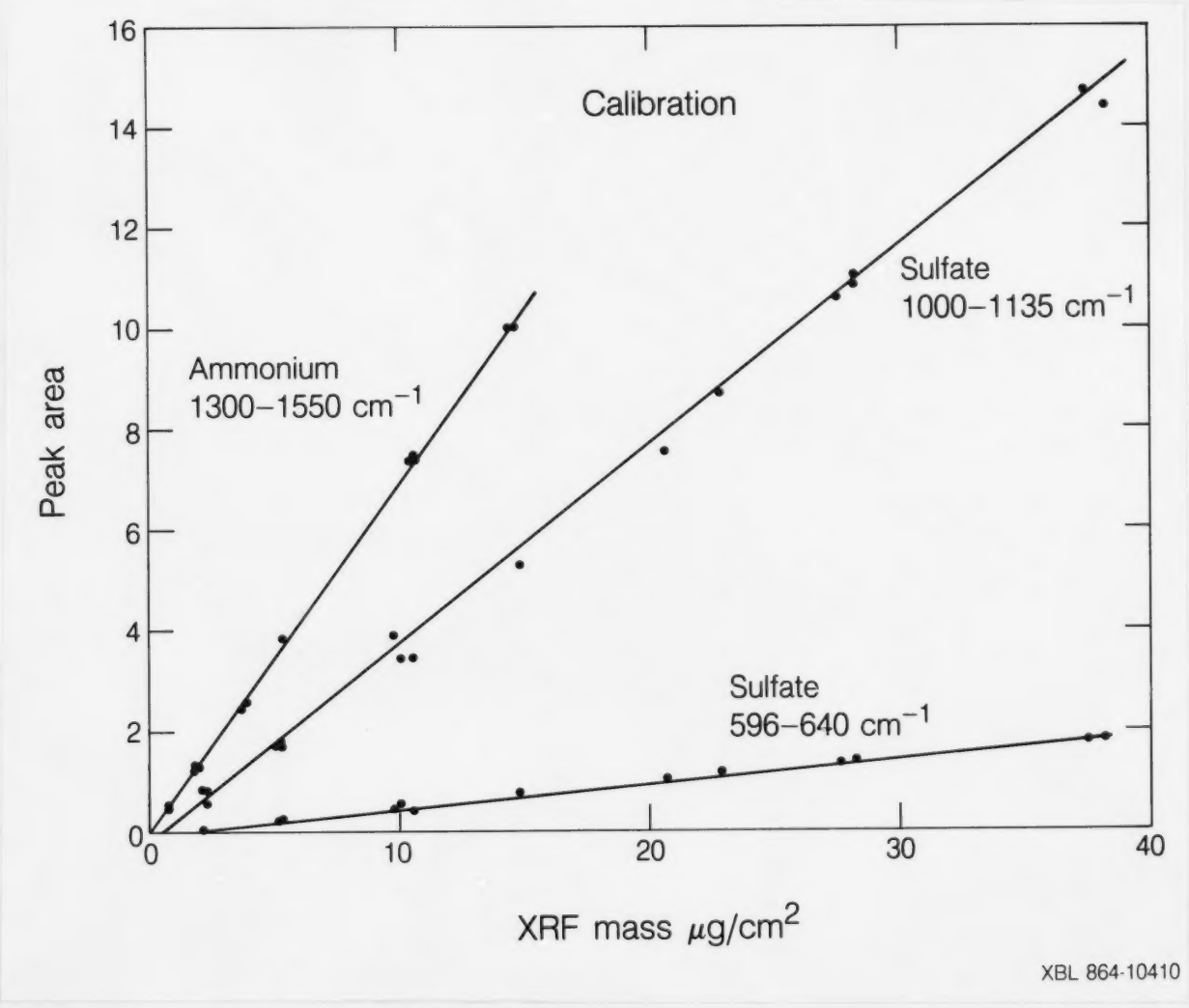

Fig. 5-2. Ammonium and sulfate calibration.

TABLE 1. Lower Limits of Detection

	Filter Concentration $\mu g/cm^2$	Ammonium Sulfate 24 hours, 21.6 m^3 Sample $\mu g/m^3$
Sulfate 596 - 640 cm^{-1}	1.70	0.86
Sulfate 1000 - 1135 cm^{-1}	0.20	0.10
Ammonium 1300 - 1550 cm^{-1}	0.15	0.20

DISCUSSION

The use of 2 μm filters and matched pre- and post-loaded filter spectra during background subtraction has realized some improvements in the lower limit of detection for ammonium and sulfate, though the improvements are not dramatic. Even though the background subtractions using 2 μm filters are much more accurate than subtractions using 1 μm filters, there is still a significant subtraction residue--relative to the sulfate absorption area--remaining. The subtraction of two spectral files with small differences in absorbance band shapes can result in derivative-like noise far in excess of what would be expected simply by statistical propagation of errors in the subtraction process. This effect can negate any signal-to-noise improvement obtained by increasing the number of measurement scans.

Figure 5-3 illustrates this effect by showing three examples of a subtraction of the two Teflon* bands in the 1135 - 1300 cm^{-1} region. This subtraction was performed on two spectra of the same blank filter after 1000 scans for each spectrum. This filter was not removed from the carousel but was simply moved out of and into the infrared beam using the automatic sample changer.

The subtraction residue or artifacts may be caused by distortion of the spectral band shapes due to light scattering effects on the detector that result from moving the filter out of and into the infrared beam between measurements. The subtraction artifacts can be worse if the spectra from two different filters are subtracted from each other because there can be significant variation in the absorption band shapes between filters. The subtraction artifacts limit the area of the 1117 cm^{-1} band that can be measured accurately to the 1000 - 1135 cm^{-1} region.

As was mentioned earlier, the subtraction problems are more severe for highly absorbing bands. The low absorption seen for the 2 μm filters in Figure 5-1 is not representative of all 2 μm filters. The filter density from different batches of filters from the manufacturer can vary significantly. While no 2 μm filters have been found to be totally absorbing, many

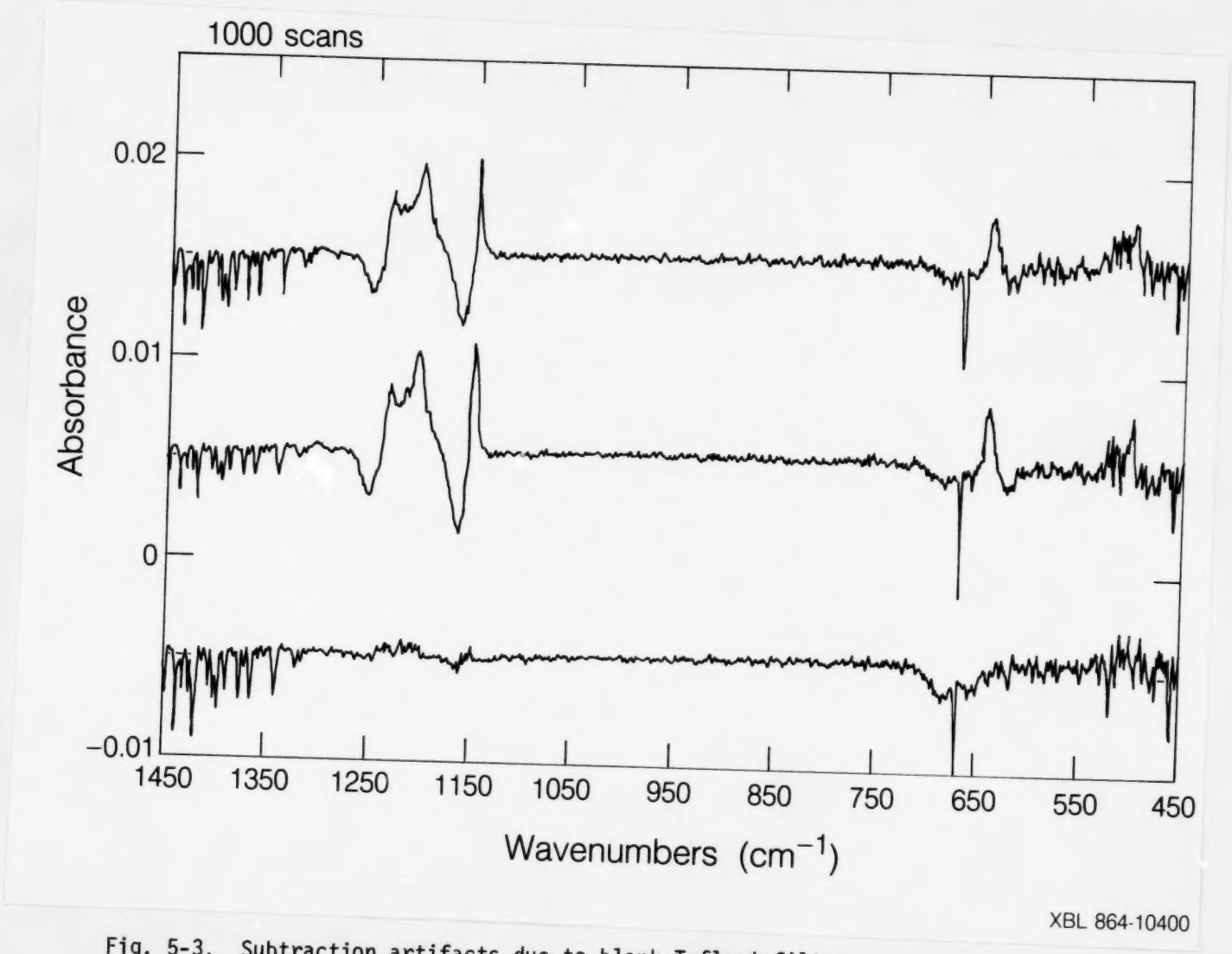

Fig. 5-3. Subtraction artifacts due to blank Teflon* filters.

filters can have maximum absorbances of up to 1.5 absorbance units. Background subtraction is much more successful in the region of the 620 cm^{-1} sulfate band because the maximum Teflon* absorbance in this region is always low.

The most significant problem associated with the subtraction artifacts is the inability to determine when the background subtraction is complete. For laboratory-generated samples this was arbitrarily defined to occur when there was zero integrated absorbance in the 1135 - 1300 cm^{-1} region of the spectrum. However, this assumes a horizontal baseline in this region for the entire filter spectrum. This is typically not the case for samples of ambi- ent particles because of absorption due to carbonaceous particles. This is discussed in more detail in the next section.

In spite of the subtraction problems encountered with Teflon* filters, no other commonly used filter media can be used for FTIR transmission spectroscopy. Glass fiber filters, paper filters, or Nylasorb* filters cannot be used with this technique because these materials cause too much scattering and absorption of the infrared radiation. It should be noted that FTIR spectroscopy has been used to analyze particles collected by impaction on ZnSe disks (Dangler, 1987) and S. Johnson (1983) has analyzed particles impacted on ATR crystals. These techniques show great promise. However, these impaction techniques are not compatible with existing instrumentation commonly used in air sampling surveys. The intent of this research was to develop methods of analysis that accomodate, as much as possible, current widely used filter media such as Teflon*.

SECTION 6

FTIR ANALYSIS OF TEFLON* FILTERS DURING THE CARBONACEOUS SPECIES METHODS INTERCOMPARISON STUDY

GENERAL INTRODUCTION

Carbonaceous particles, ammonium sulfate, and ammonium nitrate, constitute the primary particulate species found in the fine fraction (< 2.5 μm diameter) of ambient aerosols. During August of 1986, the California State Air Resources Board conducted the Carbonaceous Species Methods Intercomparison (CARB) Study in Glendora, CA. The primary purpose of the CARB study was to collect and analyze aerosol carbon species by various methods to establish a methods intercomparison data base. We participated in this study in collaboration with James Howes of Environmental Monitoring & Services, Inc. (EMSI) based in Camarillo, CA. The air samples were collected on quartz and Teflon* filters using three air samplers operating in parallel. EMSI analyzed the quartz filters for carbon and the Teflon* filters for sulfate, nitrate, ammonium, and total mass. The Teflon* filters were also analyzed for sulfate and elemental carbon at the Lawrence Berkeley Laboratory using FTIR transmission spectroscopy.

The purpose of our participation in this study was to:

1. Apply the analytical methods developed in the laboratory to the analysis of sulfate on freshly collected field filter samples.
2. Investigate the spectral interference effects of co-collected compounds, such as ammonium nitrate and carbonaceous compounds.
3. Establish the equivalence of the measurement of sulfate using FTIR transmission spectroscopy with ion chromatography (IC) analysis.
4. Develop analytical methods to quantitatively determine elemental carbon particle concentration on Teflon filters.

5. Establish the equivalence of the FTIR carbon measurement to a thermal method of carbon measurement.
6. Develop automated methods of sample manipulation and analysis for use in large sampling studies.

The results of our participation in this study are presented in this section. The discussion of the sulfate analysis of the CARB samples are presented separately from the carbon analysis.

FTIR AND ION CHROMATOGRAPHIC SULFATE ANALYSIS OF AMBIENT AIR SAMPLES

Introduction

Ambient air samples were collected by EMSI at Citrus College, in Glendora, California during the time period August 12-21, 1986. The samples were collected for the 12-hour intervals, 0800 - 2000 and 2000 - 0800 each day. Three air samplers, operated in parallel, collected 108 samples, of which 30 were analyzed by both ion chromatography (Howes, 1987) and Fourier transform infrared spectroscopy. In addition to these filters, there were five field blanks analyzed by FTIR as well. All filters were analyzed at the conclusion of the air sampling study.

Experimental Procedures

The air samplers were modified Sierra/Andersen Model 245* automated dichotomous samplers. The modification consisted of removing the virtual impactors and replacing them with identical inlets. Each inlet was equipped with a cyclone to admit particles < 2.5 μm in diameter. The regulated flow rates were approximately 24 lpm. Each channel has a rotameter to set and monitor the flow rate and a pneumatic controller to regulate the flow rate to within ± 5% of the set point for a filter pressure drop up to 35 cm Hg. The air filters were 37 mm diameter, 2 μm pore size Teflon* membrane filters supported on a polyolefin support ring. The filters were supported in circular polypropylene filter holders. The collection area of the filters is 6.38 cm^2. The filters, in their filter holders, are placed

in a circular sample carousel which is then mounted in the air sampler. All of the filters were analyzed at the conclusion of the CARB Study. The filters were analyzed nondestructively by FTIR prior to ion chromatography analysis.

Spectra of the blank Teflon filters were measured before air sampling to be used as background reference spectra. The filter spectra were measured again after air sampling and before IC analysis. Spectra were taken in dry purge air using a 2 cm^{-1} resolution over the spectral range 400 - 4600 cm^{-1} and signal-averaged for 100 scans. The sample filters were measured with the particle loaded side facing the infrared beam. The ratio of the spectra to the open-beam spectra at the time of measurement was calculated and stored as absorbance data files.

Analysis of the filter spectra for sulfate concentration requires spectral background subtraction because both sulfate bands, at 620 cm^{-1} and 1117 cm^{-1}, overlap absorption bands of the Teflon* substrate. Correction for substrate background is achieved by subtracting the spectrum of the blank filter from the spectrum of the same filter after air sampling. The resulting spectrum is due only to absorption of the collected particles and not due to absorption of the Teflon* filter. Figure 6-1 shows mid-infrared absorbance spectra from an aerosol sample obtained during the CARB study on August 14-15, 1986 during the 2000 - 0800 sampling interval. The dashed line is the spectrum of the blank Teflon* filter before sampling. The absorbance scale for this spectrum is on the right side of the figure. The solid line is the spectrum of the collected aerosol particles after subtraction of the Teflon* filter background spectrum. The absorption scale for this spectrum is on the left side of the figure. The ammonium, nitrate, and sulfate absorption bands are indicated. The overlap of the sulfate and Teflon* absorption bands can be seen by comparing the two spectra in Figure 6-1.

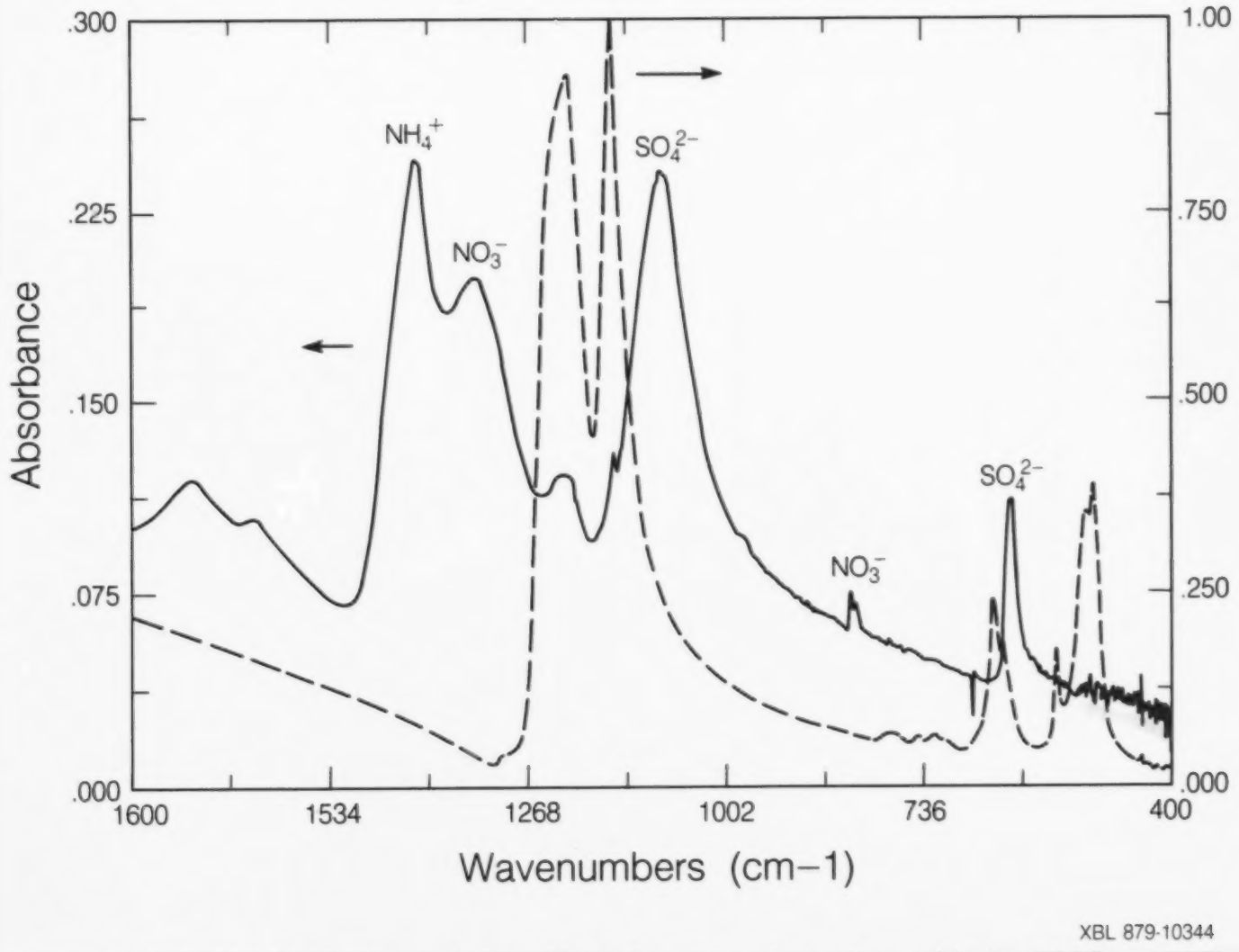

Fig. 6-1. The background corrected infrared spectrum of an ambient aerosol sample (solid line) and the blank Teflon* filter before sampling (dashed line).

The subtraction, on the Nicolet 5DXB FTIR, is performed according to the following formula:

RESULT SPECTRUM = SAMPLE SPECTRUM - FCR*REFERENCE SPECTRUM

where the variable FCR is a scale factor approximately equal to one. The variable FCR is determined by an iterative procedure. The subtraction is complete when all of the absorption due to the reference background has been nulled. This requires that there be a region where the absorbance due only to Teflon* can be measured. In spectra of actual ambient filter samples there are no regions free of absorption due to collected compounds. Carbon compounds, organic and inorganic, absorb over the entire mid-infrared region of 400 - 4600 cm^{-1}. This means that the criteria for the determination of the completion of the background subtraction must account for the overlapping carbon absorption. This is distinct from the earlier case of laboratory standards where carbon absorption was not present.

A program was written for the FTIR to analyze ambient particles collected on Teflon* filters. The program automatically subtracts the reference spectrum from the sample spectrum for each filter. The subtraction criteria are described as follows: in the region 400 - 700 cm^{-1} the carbon absorbance is assumed to be linear with increasing wavenumber. Since the Teflon* band at 514 cm^{-1} does not interfere with any sulfate, nitrate, or ammonium bands, this band can be subtracted to yield a linear background due only to the carbon absorption spectrum. Figure 6-2 illustrates the background subtraction procedure. The carbon absorption in the region of the Teflon* band is assumed to be a linear interpolation of the carbon absorption on both sides of the 514 cm^{-1} Teflon* band. This interpolation is calculated to be the least squares fit line to the data in the region 567 - 572 cm^{-1} and 447 - 480 cm^{-1} (regions A and B in Figure 6-2). The FCR value is varied until the area of the 514 cm^{-1} band is zero above the carbon spectrum. After each iteration of the FCR value a linear least squares fit line is calculated for the data in regions A and B. The area of the spectrum above this line and between regions A and B is calculated. In Curve 1 a value of FCR = 1.1000 subtracts too large a multiple of the Teflon* absorption band resulting in a negative area. FCR is decreased in Curves 2

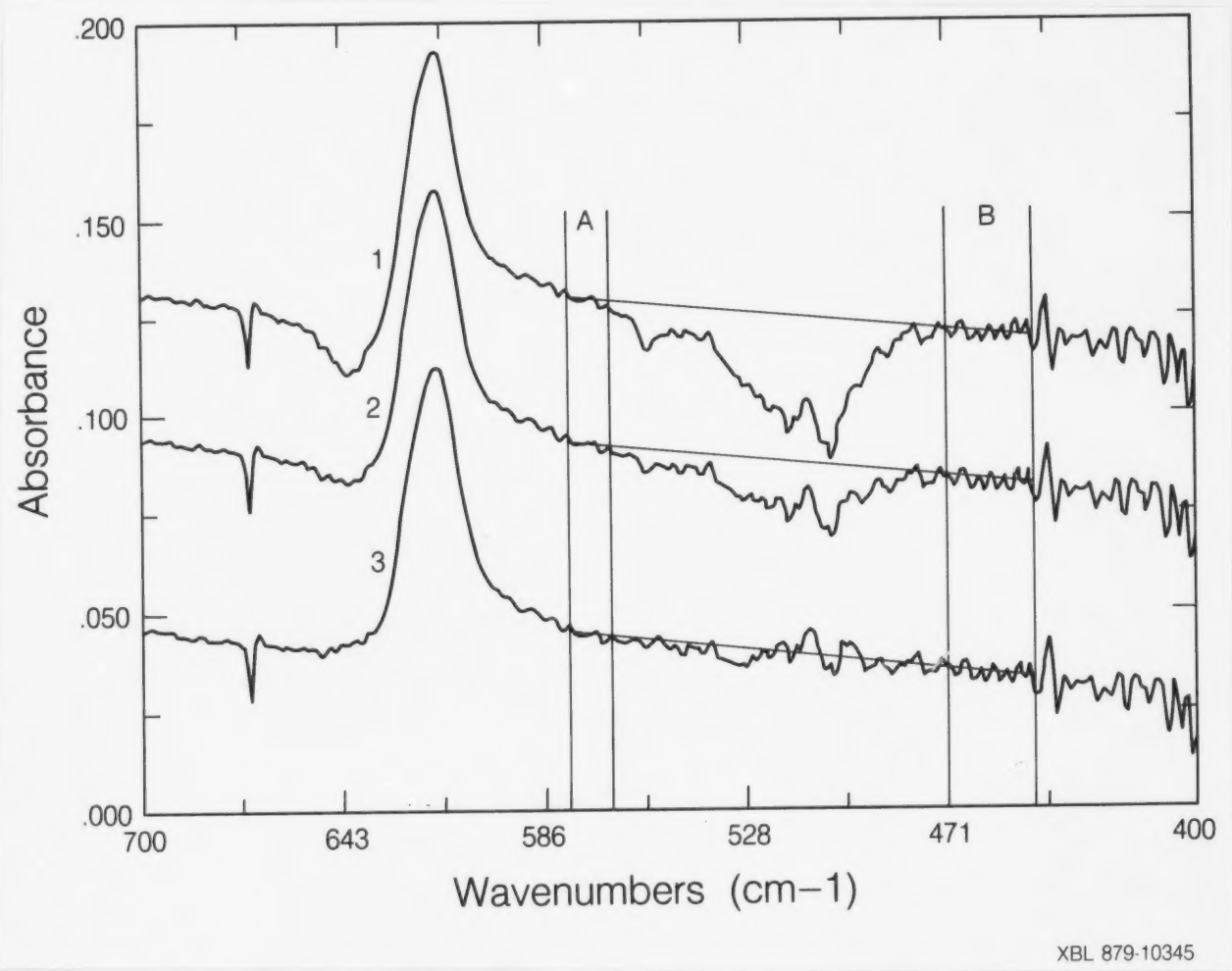

Fig. 6-2. Determination of the proper subtraction of the Teflon* absorption band in the vicinity of the 620 cm^{-1} sulfate band. A least squares fit line is calculated from data in regions A and B.

and 3 until the area above the curve is zero as is true for Curve 3 in Figure 6-2.

Following subtraction of the background due to the Teflon* substrate, the area of the sulfate bands above the carbon absorption baseline was calculated for the bands at 620 cm^{-1} and 1117 cm^{-1}. The baseline under the 620 cm^{-1} absorption band was calculated to be the least squares fit line to the absorption data between 660 - 670 cm^{-1} and 565 - 590 cm^{-1}. The baseline under the 1117 cm^{-1} sulfate absorption band was calculated to be the least squares fit line to the absorption data in the region 680 - 815 cm^{-1}. The sulfate band areas were used to calculate a sulfate filter concentration from a sulfate calibration equation given in Section 4.

Calibration standards were prepared by depositing particles of ammonium sulfate on blank Teflon* filters. The particles were generated using a constant output collision nebulizer (TSI model 3075) (May, 1973). The ammonium sulfate solution was prepared by mixing 2 mg/mL of the reagent grade compound with water. The particles from the nebulizer are dried with a silica diffusion dryer and are charge neutralized in a Kr-85 diffusion discharger. The particles from the aerosol generator were deposited on the filter through the fine particle (< 2.5 μm diameter) inlet of a dichotomous air sampler. The sulfate concentration on the filters was inferred from sulfur measurements using x-ray fluorescence analysis. The sulfate concentration of the calibration standards varied between 2 - 38 μg cm^{-2}. Independent calibration curves were calculated based on the band area associated with the sulfate absorbance bands at 1117 cm^{-1} and 620 cm^{-1} respectively. There is no overlapping soot background to consider in the analysis of the laboratory standards but the same algorithm was used to perform background subtraction and area calculations as was used for the field samples.

Following the FTIR analysis, the filters were sent to EMSI for ion chromatography analysis. The sulfate analysis (Howes, 1987) was performed on a Dionex* model 10 ion chromatograph with an anion separator column and an anion fiber suppressor. One hundred microliters of ethyl alcohol was pipetted onto each filter to promote wetting during the extraction procedure. The

Teflon* filters were extracted in 15 mL of deionized water for 30 minutes in an ultrasonic bath. Extraction reagent blanks were prepared for every 30 samples. Filter spikes for NO_3, SO_4, Cl^-, and NH_4 were prepared for every 30 samples. For the sulfate levels found on the ambient filter samples the accuracy of the IC analysis was 2% with a precision of ± 2%. Assuming a 5% sampling error, the overall IC measurement error is approximately 5.4%.

Results and Discussion

A number of problems are encountered when we apply the FTIR analysis protocol developed for laboratory-generated aerosols to ambient aerosol samples. The ambient spectrum in Figure 6-1 illustrates the difficulties in the analysis of sulfate due to interferences from co-collected compounds on the filters. The major components of the fine fraction of ambient air particles collected on Teflon* air filters are ammonium sulfate, ammonium nitrate, and both elemental and organic carbonaceous particles. Distinct ammonium, sulfate, nitrate, and Teflon* bands are visible in the spectra of Figure 6-1. Each sulfate absorption band is seen to overlap Teflon* bands. The nitrate absorption band overlaps both a Teflon* band and the ammonium band. Carbonaceous particles absorb continuously across the entire spectrum and can be seen as the nonzero baseline gradually rising in absorption with increasing wavenumber.

To achieve an accurate band integration two steps must be accomplished. First it is necessary to achieve a correct background subtraction of the spectrum of the blank Teflon* filter from that of the sample filter. Second, the carbon baseline must be estimated underneath the sulfate band.

Two difficulties were encountered in the attempt to achieve an accurate area integration of the 1117 cm^{-1} sulfate band which were not encountered during the development of analytical techniques in the laboratory. The first is attributable to absorption in this region due to carbon compounds. Unlike the linear behavior of the carbon spectrum across the 514 cm^{-1} Teflon* band, the carbon spectrum cannot be linearly interpolated across the 1000 - 1300 cm^{-1} region. This can be seen in Figure 6-1 by noting that the carbon baseline increases linearly between 400 - 1000 cm^{-1} but it has decreased in

absorbance at 1525 cm^{-1} just above the ammonium band. Infrared measurements of propane soot deposited on KBr pellets also show variation in the spectra of soot in this region consistent with the spectra of the particles collected in the CARB samples. There is also evidence in the literature of this structure in the infrared spectra of elemental carbon (Friedel, 1970; Akhter, 1985). It should also be noted that the carbon absorbance in Figure 6-1 is due to both elemental and organic carbon. Functional group absorption due to organic compounds could also influence the variation of total absorbance in this region.

The second difficulty is due to the inability to determine the point at which the Teflon* bands in the 1000 - 1300 cm^{-1} region have been completely nulled in the subtraction process. Laboratory experiments on blank filters indicate that the scale value (FCR) that nulls the 514 cm^{-1} Teflon* band does not necessarily null the Teflon* bands in the 1000 - 1300 cm^{-1} region. Figure 6-1 shows that the nitrate band also overlaps the Teflon* bands. Since the nitrate and carbon spectra are variable and unknown it is impossible to achieve a successful background subtraction because there are no interference free Teflon* bands in this region to serve as a background reference in the subtraction process and the structure of the carbon absorption baseline is unknown.

In a previous study (McClenny, et al., 1985), the difficulty of completely subtracting the strong Teflon* absorbance bands in the 1000 - 1300 cm^{-1} region for 1 μm pore size filters was described. It was suggested that this problem might be mitigated by use of less absorbing 2 μm filters. The subtraction difficulties encountered using 1 μm pore size filters can be attributed to the fact that absorbance subtraction is extremely sensitive to small deviations in the absorbance values of the spectra (Hirschfeld, 1975a, 1975b, 1976) particularly for strongly absorbing bands. The 2 μm pore size filters do not absorb as strongly as the 1 μm pore size filters because of the greater mass of the 1 μm filters. While it is true that the subtractions are better for the 2 μm filters, the ultimate limitation in the analysis of ambient filters using the 1117 cm^{-1} sulfate band is not the fundamental

difficulties of background subtraction, but the uncontrolled variability of spectra due to co-collected nitrate and carbon found in ambient air samples.

The background subtraction techniques previously described for the 620 cm^{-1} region were applied to the samples collected during the CARB study. Figure 6-3 is a histogram of data for the daily sulfate concentrations determined by both ion chromatography and Fourier transform infrared spectroscopy. The FTIR sulfate concentrations in Figure 6-3 are based on the area measurement of the weak sulfate absorption band at 620 cm^{-1}. The sampling periods are labeled for days 2 - 10. The daytime sampling periods are labeled with the number 6 and the nighttime sampling periods are labeled with the number 7. The first sampling period began during the day of August 12, 1986. All measurements are corrected to standard conditions of 25°C and 760 mm Hg.

It is clear from Figure 6-3 that both the FTIR and the IC measurements follow the same trends throughout the entire study period. From the beginning of the study through day 6 the agreement between the FTIR and IC measurements is very good. The differences between the two measurements is less than 10%. From day 7 through the end of the study almost all of the FTIR measurements are 2 $\mu g/m^3$ lower than the IC measurements. Since the absolute sulfate concentrations were low during this period of the study, the relative differences between the FTIR and IC measurements is quite high, exceeding 100% in some cases. All of the filters, both the calibration filters and the CARB study samples, were analyzed by the same objective criterion in the automated background subtraction program written for the FTIR computer. The consistently low FTIR measurements might indicate a bias in the calibration, but this is ruled out because there is no such bias in the measurements during the first part of the study. The absolute error becomes greater as the concentration of the sulfate in the atmosphere decreased indicating a high lower limit of detection for the FTIR method of analysis. In fact measurements of the field blanks showed a large variation in the area measured in the 620 cm^{-1} band region. A calculation, based on the calibration spectra and the five field blanks from the CARB study, showed that the lower limit of detection for the determination of sulfate in the atmosphere

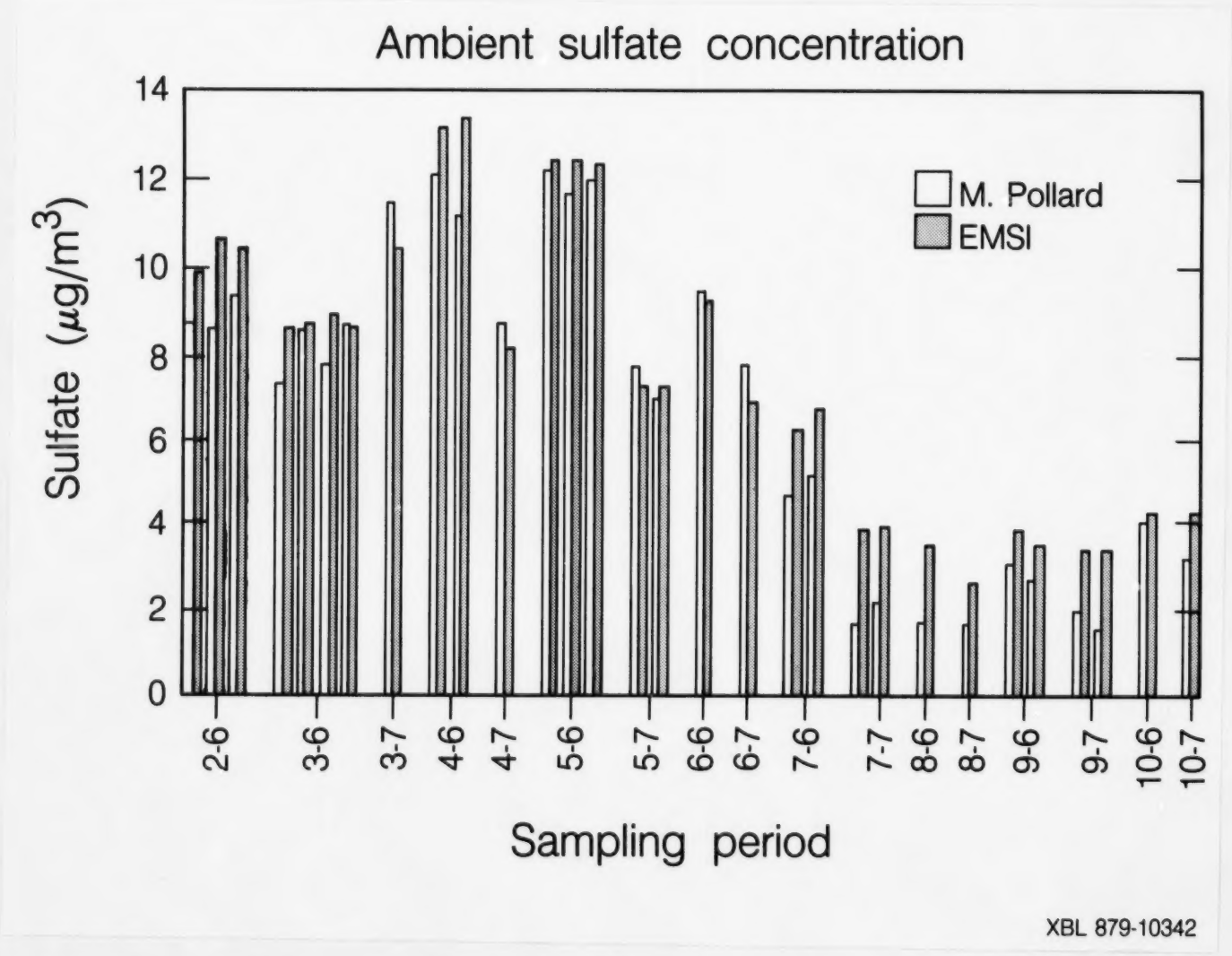

Fig. 6-3. A comparison of ambient sulfate concentrations measured during the CARB study.

was 5.8 $\mu g/m^3$. The last ten samples measured by ion chromatography were below the calculated lower limit of detection for the FTIR analysis using the 620 cm^{-1} absorption band.

Sulfate concentrations were also calculated using the 1117 cm^{-1} band after background subtraction based on the 514 cm^{-1} Teflon* band. The 514 cm^{-1} Teflon* band was used because of the difficulties of subtracting the Teflon* bands in the 1000 - 1300 cm^{-1} region described earlier. A carbon baseline underneath the sulfate band was calculated based on an interpolation of the carbon data in the region 680 - 815 cm^{-1}. There was poor agreement between ambient sulfate concentrations calculated using this band and with the ion chromatography analysis indicating that the 514 cm^{-1} Teflon* absorbance band is too far from the 1117 cm^{-1} sulfate band to provide an adequate background subtraction as was discussed earlier. The results for the 1117 cm^{-1} sulfate band are not presented here.

The large variation in the field blank measurement values indicated problems that can lead to a high lower limit of detection. One possible source of the variation in the field blanks is the scattering effects due to filter orientation. Electron micrographs of Teflon* filters show that the filters do not have a uniform fibrous structure but rather a banded structure consisting of thick Teflon* fibers with smaller interconnecting Teflon* fibers. The thick fibers defined a specific orientation for each filter. There is significant scattering due to the blank Teflon* filter above 1500 cm^{-1}. The effects of filter orientation on measurements at the 620 cm^{-1} sulfate band region were investigated by measuring the spectra of a single blank filter at various relative orientations from 0 - 360°. It was determined that the variation in the measured area for subtracted spectra of randomly oriented filters was five times that for subtracted spectra where filter orientation was maintained throughout the analysis. The areas were determined with the same automatic background subtraction program used to analyze the calibration spectra and the CARB field samples. Maintaining filter orientation throughout the analysis procedure during the CARB study would lower the lower limit of detection to 1 - 2 $\mu g/m^3$. There are distinctive features to the subtraction spectra of filter measured at 90° relative

orientation to each other. These features were observed in a number of the subtraction spectra of the CARB study samples confirming that this problem does exist in the analysis of the CARB study samples.

There is good correlation between the sulfate measurement obtained by integrating the 620 cm^{-1} sulfate band and sulfate measured by ion chromatography. Figure 6-4 is a scatter plot of the FTIR sulfate measurements and the ion chromatography sulfate measurements on the thirty ambient air filters as shown in Figure 6-3. The regression line in Figure 6-4 is calculated from the twenty data points above the FTIR detection limit. The regression equation has a slope = 0.92, σ_b = 0.1, an intercept = 1.26, σ_a = 0.94, and a linear correlation coefficient of r = 0.912. The cause of the significant non-zero intercept is unknown.

Conclusions

There is good agreement for measurements of particulate sulfate on Teflon* air filters using Fourier transform infrared transmission spectroscopy and ion chromatography analysis. The sensitivity of the FTIR absorbance measurements were not adequate to accurately measure all of the samples collected during the CARB study. The lower limit of detection, based on the 620 cm^{-1} band, could be improved by a factor of 4 - 5 by maintaining filter orientation during measurement of the reference and sample spectra. This should also improve the accuracy of measurements above the lower limit of detection as well. An improvement of this magnitude in the detection limit would have brought the FTIR measurement sensitivity low enough to accurately measure ambient concentrations throughout the CARB study. The stronger sulfate absorbance band at 1117 cm^{-1} could not be used because of spectral interferences of components co-collected on the filters and the practical limitations of spectral absorbance subtraction. The suitability of this technique, as well as all techniques, depends on the sampling scheme used. Longer sampling times and higher sampler flow rates would provide adequate samples for accurate measurements for typical ambient concentrations.

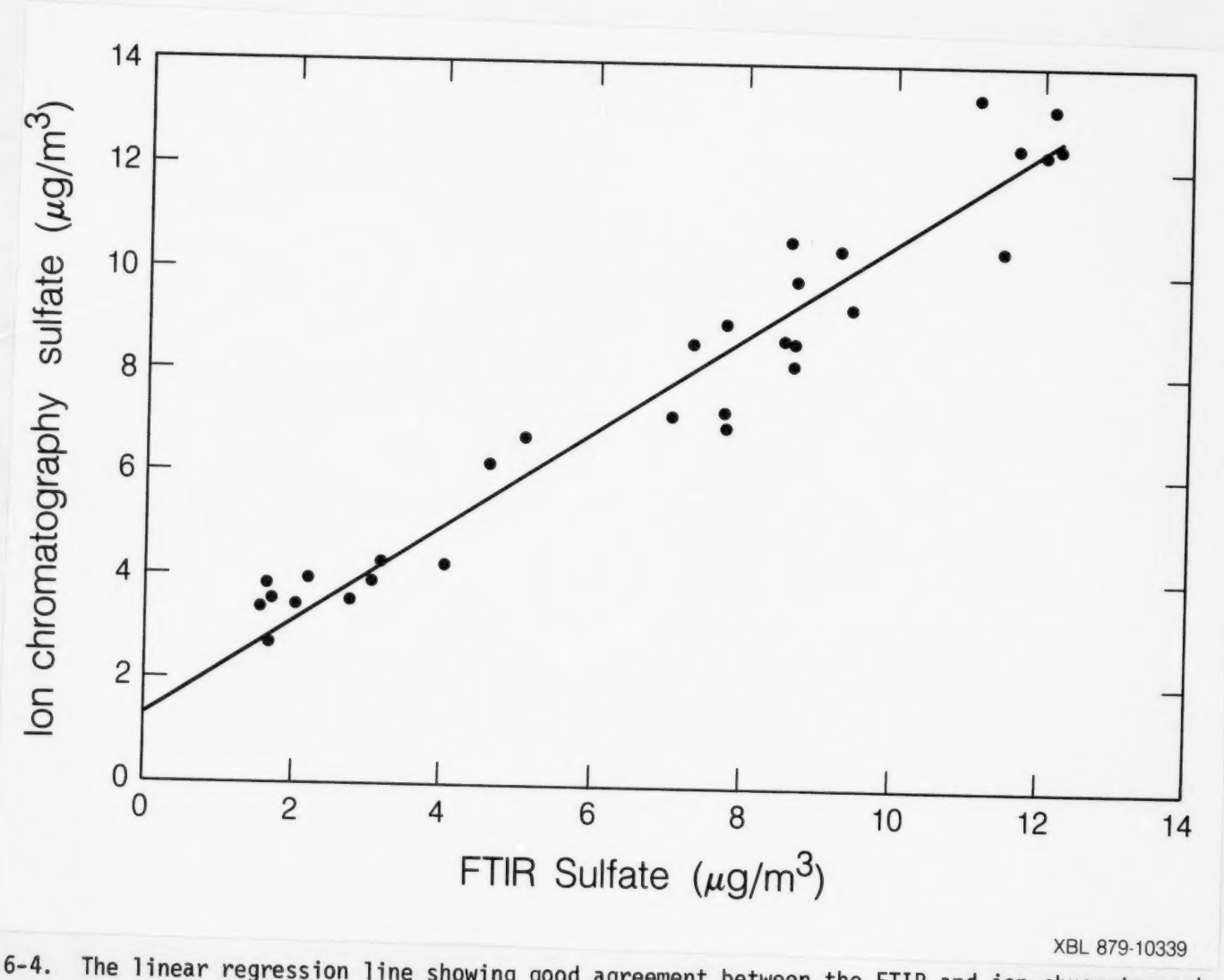

Fig. 6-4. The linear regression line showing good agreement between the FTIR and ion chromatography measurements of sulfate concentrations in the atmosphere.

ANALYSIS OF CARBONACEOUS PARTICLES ON TEFLON* FILTERS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

Introduction

Carbonaceous particles, along with ammonium sulfate and ammonium nitrate, constitute the primary particulate species in the fine fraction (< 2.5 μm diameter) of ambient aerosols. Particles in this size range scatter visible light very efficiently contributing to visibility degradation. In addition, carbon particles are the primary light absorbing species in ambient aerosols and they play an important role in the radiative heat balance of the atmosphere. They may also pose a long term health hazard (Daisey, 1980). Carbonaceous particles are a complex mixture of many different compounds but they can generally be divided into elemental and organic fractions each of which can be associated with both anthropogenic and natural sources (Novakov, 1984). Elemental carbon is produced solely in combustion processes. The results for the carbon particle analysis for samples collected during the CARB study will be presented. Two methods of analysis for elemental carbon particles, collected concurrently on quartz and Teflon* filters, are compared.

A variety of analytical methods are used to determine the concentration of organic and elemental carbon collected on air filters. The most widely used procedures for carbon aerosol analysis are thermal methods that determine both volatile (organic) and non-volatile (elemental) carbon (Huntzinger, et al., 1982; Cadle, 1982) collected on quartz filters. Organic carbonaceous compounds can also be analyzed with solvent extraction methods (Grosjean, 1975). Nonextractable carbon is assumed to be elemental carbon. Both thermal and solvent extraction methods destroy the filter sample during the analysis. Simple, rapid, and nondestructive optical techniques can be used to measure elemental carbon independently of organic carbon (Lin, 1973; Rosen, 1983). These techniques assume that the absorption of light is due predominantly to elemental carbon since it can be shown that carbon particles absorb much more visible light than any other major aerosol species present in the ambient atmosphere.

Experimental Procedures

Elemental carbon standards were prepared by depositing propane soot on Teflon* filters using a dichotomous air sampler. The soot deposition on the filters in the fine fraction (< 2.5 μm diameter) channel of the sampler was determined gravimetrically on a Sartorius model 4503 MP6* microbalance (sensitivity 1 μg). Each filter was weighed five times before and after loading with propane soot. The masses of the soot standards ranged from 12 - 80 μg corresponding to areal densities of 2 - 15 $\mu g/cm^2$.

The quartz filters were analyzed by EMSI using a modified Dorhman* carbon analyzer and a Horiba Model PIR 2000* nondispersive infrared (NDIR) CO_2 detector. A 0.64 cm (0.25 inch diameter) punch from the exposed area of a quartz filter was placed in the analyzer. Organic compounds were volatilized (but not oxidized) in helium carrier gas to 600°C and transported downstream to a zone packed with manganese dioxide (MnO_2) and heated to 350°C. Here the gaseous hydrocarbon species are converted to CO_2 which is then detected by the NDIR CO_2 detector. The remaining elemental carbon on the quartz punch is heated to 750°C in a carrier gas of helium containing 2% oxygen. The evolved CO_2 is detected with the NDIR CO_2 detector.

Results and Discussion

The mid-infrared (400 - 4600 cm^{-1}) absorption spectra of ambient aerosols includes information useful for the determination of the concentration of soot, sulfate, nitrate, and ammonium collected on Teflon* filters. The infrared spectra of ambient aerosol particles has been reported previously (Cunningham, 1974; McClenny, et al., 1985; Pollard, 1986). Figure 6-1 shows mid-infrared absorbance spectra from an aerosol sample obtained during the CARB study on August 14-15, 1986 during the 2000 - 0800 sampling interval. The dashed line is the spectrum of the blank Teflon* filter before sampling. The absorbance scale for this spectra is to the right of the figure. The solid line is the spectrum of the collected aerosol particles after subtraction of the background Teflon* filter spectrum. The absorbance scale for this spectrum is on the left side of the figure. The functional absorbance

bands for sulfate, nitrate, and ammonium have been identified. The infrared spectrum of elemental carbon is predominantly continuous across the entire region shown in Figure 6-1. Some weak broad absorbance bands due to surface functional groups have been identified in other studies (Akhter, 1985; Friedel, 1970; Mattson, 1969) of carbon soots.

The organic component of soot consists of a complex mixture of many compounds with overlapping infrared spectra (Boone, 1986). Some of the organic functional group infrared absorbance bands have been identified (Dangler, et al., 1987) for ambient aerosols. In our spectra of aerosols on Teflon* filters collected during the CARB study, distinct aliphatic absorbance bands at 2920 cm^{-1} and 2853 cm^{-1} could be seen in 17 filter spectra. Figure 6-5 is a spectrum obtained from one of these filters. The aliphatic absorbance bands are superimposed on a broad ammonium band between 2800 - 3400 cm^{-1} (Hertzberg, 1964). Organic absorbance bands in other regions of the spectrum have not been observed. Many of these could be obscured by the ammonium, nitrate, sulfate, and Teflon* absorbance bands in the 1000 - 1550 cm^{-1} region. The spectra in which the aliphatic absorbance bands have been observed are identified in Table 2. The organic bands are most distinct when the relative ammonium concentration is low. This was the situation for the samples collected toward the end of the CARB study. No attempt was made to quantitatively determine aliphatic carbon concentrations on the filters.

The presence of the relatively strong aliphatic absorbance bands suggested that other functional group absorbances may interfere with measurements made for other components in other regions of the infrared spectrum. In order to quantitatively determine elemental carbon, a region of the infrared spectrum where organic compounds do not absorb should be chosen for the elemental carbon analysis. A number of articles have been written describing organic compounds that have been identified in ambient aerosols (Daisey, 1980; Van Vaeck, 1978). Figure 6-6 is an absorbance map (Aldrich, 1978) of some classes of organic compounds such as aliphatic hydrocarbons, carboxcylic acids, and nitrogen-containing aromatics found in ambient aerosols. In this study the region 650 - 666 cm^{-1} was chosen to measure elemental carbon because:

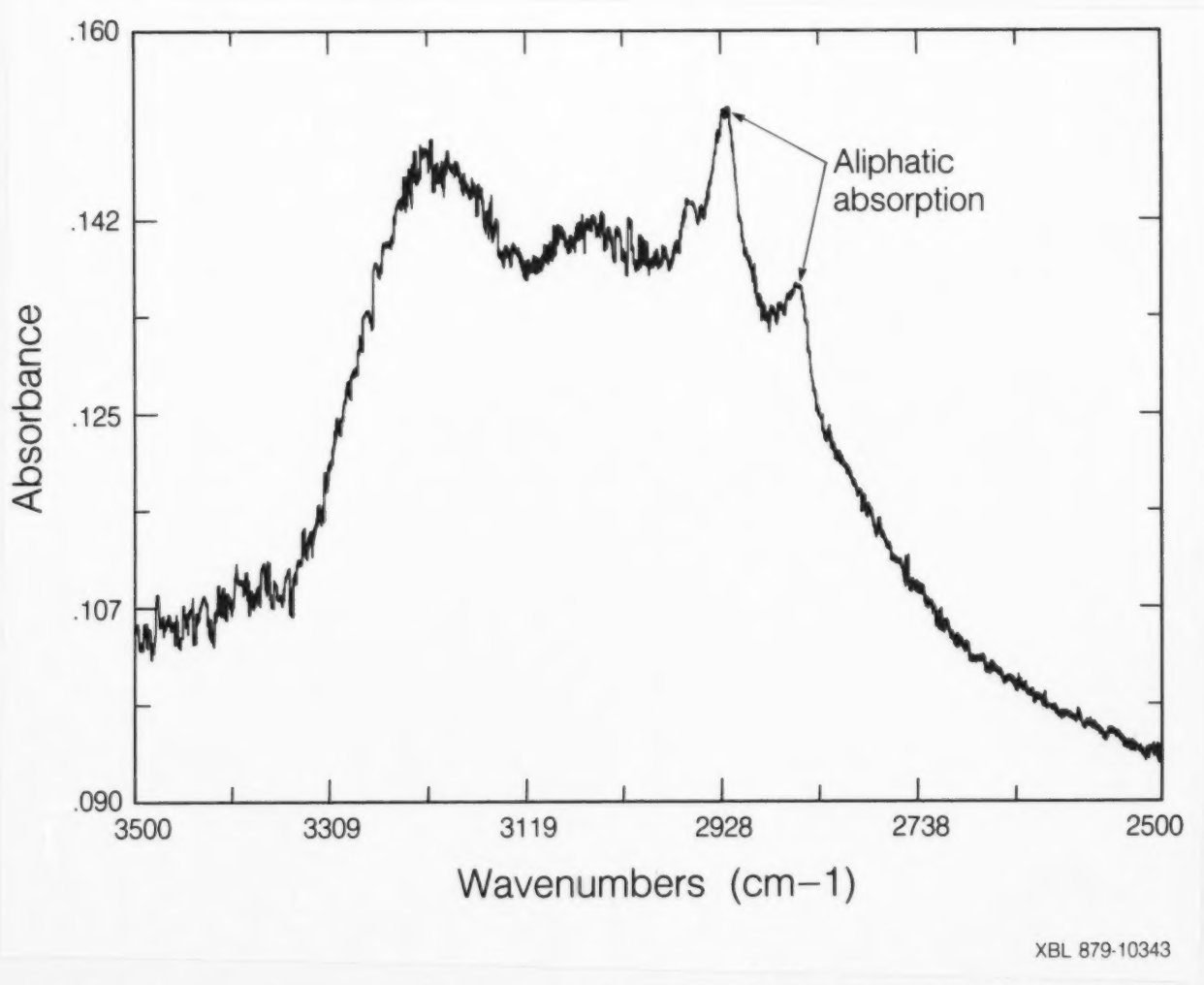

Fig. 6-5. The infrared spectrum of an ambient aerosol sample showing the aliphatic absorption bands at 2920 cm^{-1} and 2853 cm^{-1} superimposed on a broad ammonium absorption band.

TABLE 2. Results of Carbon Particle Analysis for the CARB Study

Sampling Date	Time	Sampler[a]	Sampled Volume m3	EMSI[c] Organic Carbon[b]	EMSI[c] Elemental Carbon[b]	LBL Elemental Carbon[d] Thermal Calibration[b]	LBL Elemental Carbon[d] Propane Calibration[b]
	0806-2000	1 A	16.56			7.28	14.94
	0806-2000	1 B	16.24	12.11	6.16		
8/12	0806-2000	2 A	16.56	11.74	7.70		
	0806-2000	2 B	16.56	11.89	7.36		
	0806-2000	3 A	16.56			9.29	17.68
	0806-2000	3 B	16.40			7.76	15.53
	2127-0800	1 B	14.41	5.52	3.10		
8/12	2127-0800	2 A	14.49	6.04	3.74		
8/13	2127-0800	2 B	14.31	5.86	3.10		
	1014-2000	1 B	13.43			3.57	11.21
	1035-2000	2 A	13.00			5.15	14.61
8/13	1035-2000	2 B	13.00	14.05	6.11		
	0932-2000	3 A	14.45			5.47	13.69
	0932-2000	3 B †	14.45			8.02	18.07
	2011-0705	1 B	14.90	7.11	3.81		
8/13	2011-0800	2 A †	16.32			11.39	21.13
8/14	2011-0800	2 B	16.32	5.64	4.05		
	0830-2000	1 A †	16.26			8.17	16.29
	0830-2000	1 B	16.10	15.20	7.25		
8/14	0805-2000	2 A	17.01	14.04	9.58		
	0805-2000	2 B	16.85	14.59	8.72		
	0805-2000	3 A	17.01			9.69	17.79
	2010-0809	1 A	16.85			4.10	9.71
	2010-0809	1 B	16.60	6.27	4.11		
8/14	2010-0809	2 A	17.27	6.02	3.92		
8/15	2010-0809	2 B	16.77	4.35	4.42		
	0825-2000	1 A	6.16			6.78	14.26
	0825-2000	1 B	16.00	12.94	7.58		
8/15	0825-2000	2 A	16.40			6.23	13.21
	0825-2000	2 B	15.68	13.60	7.31		
	0825-2000	3 A	16.08			6.33	13.63
	2014-0800	1 A †	16.27			2.65	7.84
8/15	2014-0800	1 B	16.15	5.06	3.23		
8/16	2014-0800	2 A	16.80			3.36	8.65
	2014-0800	2 B	16.31	4.65	2.43		
	0811-2000	1 A	15.94			4.56	10.99
8/16	0811-2000	1 B	15.86	13.92	6.48		
	0811-2000	2 A	16.39	11.56	6.30		
	0811-2000	2 B	16.02	13.59	6.58		

TABLE 2. continued

Sampling Date	Time	Sampler[a]	Sampled Volume m^3	EMSI[c] Organic Carbon[b]	EMSI[c] Elemental Carbon[b]	LBL Elemental Carbon[d] Thermal Calibration[b]	LBL Elemental Carbon[d] Propane Calibration[b]
8/16	0811-2000	3 A	16.31	11.20	4.22		
	0811-2000	3 B	15.85	11.24	5.50		
	2010-0800	1 A	16.41			3.37	8.88
	2010-0800	1 B	16.25	9.57	4.14		
8/16	2010-0800	2 A	15.93	8.09	4.58		
8/17	2010-0800	2 B	15.69	9.48	3.66		
	2010-0800	3 A	16.65	6.31	2.96		
	2010-0800	3 B	15.77	7.83	2.91		
	0808-2002	1 A †	16.50			3.74	9.38
	0808-2002	1 B	16.34	13.54	3.97		
8/17	0808-2002	2 A	16.02			6.14	13.38
	0808-2002	2 B	15.77	13.95	4.30		
	0808-2002	3 A	16.75	12.74	3.84		
	0808-2002	3 B	15.86	12.76	3.71		
	2009-0800	1 A †	16.33			.71	4.87
8/17	2009-0800	1 B	16.24	6.85	1.94		
	2009-0800	2 A †	16.00			.74	5.02
8/18	2009-0800	2 B	15.61	7.23	2.13		
	2009-0800	3 A	16.49	5.17	2.61		
	2009-0800	3 B	15.92	5.56	2.00		
	0806-2000	1 A †	15.60			5.05	12.00
	0806-2000	1 B	16.39	12.31	4.19		
8/18	0806-2000	2 A	15.75	9.16	4.27		
	0806-2000	2 B	15.35	10.43	2.94		
	0806-2000	3 A	16.23	9.34	4.18		
	0806-2000	3 B	15.12	8.32	3.70		
	2009-0800	1 A	16.14			1.78	6.57
	2009-0800	1 B	16.14	6.35	1.62		
8/18	2009-0800	2 A	15.90	6.68	1.68		
8/19	2009-0800	2 B	15.35	7.51	1.42		
	2009-0800	3 A	14.88	8.00	1.84		
	2009-0800	3 B	14.88	7.56	1.73		
	0812-2000	1 A †	16.07			4.89	11.41
8/19	0812-2000	1 B	16.07	10.74	3.65		
	0812-2000	2 A †	15.83			5.08	11.88
	0812-2000	2 B	15.28	10.54	3.38		
	0812-2000	3 A	14.81	11.00	3.60		
	0812-2000	3 B	14.81	9.08	3.28		
8/19	2010-0800	1 A †	16.15			2.84	8.20
8/20	2010-0800	1 B	16.07	9.12	3.17		

TABLE 2. continued

Sampling Date	Time	Sampler[a]	Sampled Volume m^3	EMSI[c] Organic Carbon[b]	EMSI[c] Elemental Carbon[b]	LBL Elemental Carbon[d] Thermal Calibration[b]	LBL Elemental Carbon[d] Propane Calibration[b]
8/19	2010-0800	2 A †	16.31			2.31	7.31
8/20	2010-0800	2 B	16.15	9.09	3.09		
	2010-0800	3 A	14.27	9.70	3.04		
	2010-0800	3 B	14.19	8.80	2.67		
	0808-2000	1 A	16.09			8.62	17.16
	0808-2000	1 B	16.25	12.07	7.50		
8/20	0808-2000	2 A	16.17	12.93	6.59		
	0808-2000	2 B	15.69	12.22	5.60		
	0808-2000	3 A	13.23	13.99	5.50		
	0808-2000	3 B	12.72	12.62	6.05		
	2010-0800	1 A	16.29			4.67	10.92
	2010-0800	1 B	16.13	9.94	4.43		
8/20	2010-0800	2 A	16.13	9.87	5.47		
	2010-0800	2 B	15.81	10.55	4.03		
8/21	2010-0800	3 A	13.72	10.86	3.98		
	2010-0800	3 B	12.83	9.66	3.42		

†Distinct aliphatic absorption bands

[a]Three dichotomous samplers were used. The A and B refer to the two separate inlets in each sampler.

[b]All measurements in $\mu g/m^3$.

[c]EMSI organic and elemental carbon on quartz filters by thermal combustion analysis.

[d]LBL measured elemental carbon on Teflon* filters using infrared absorbance.

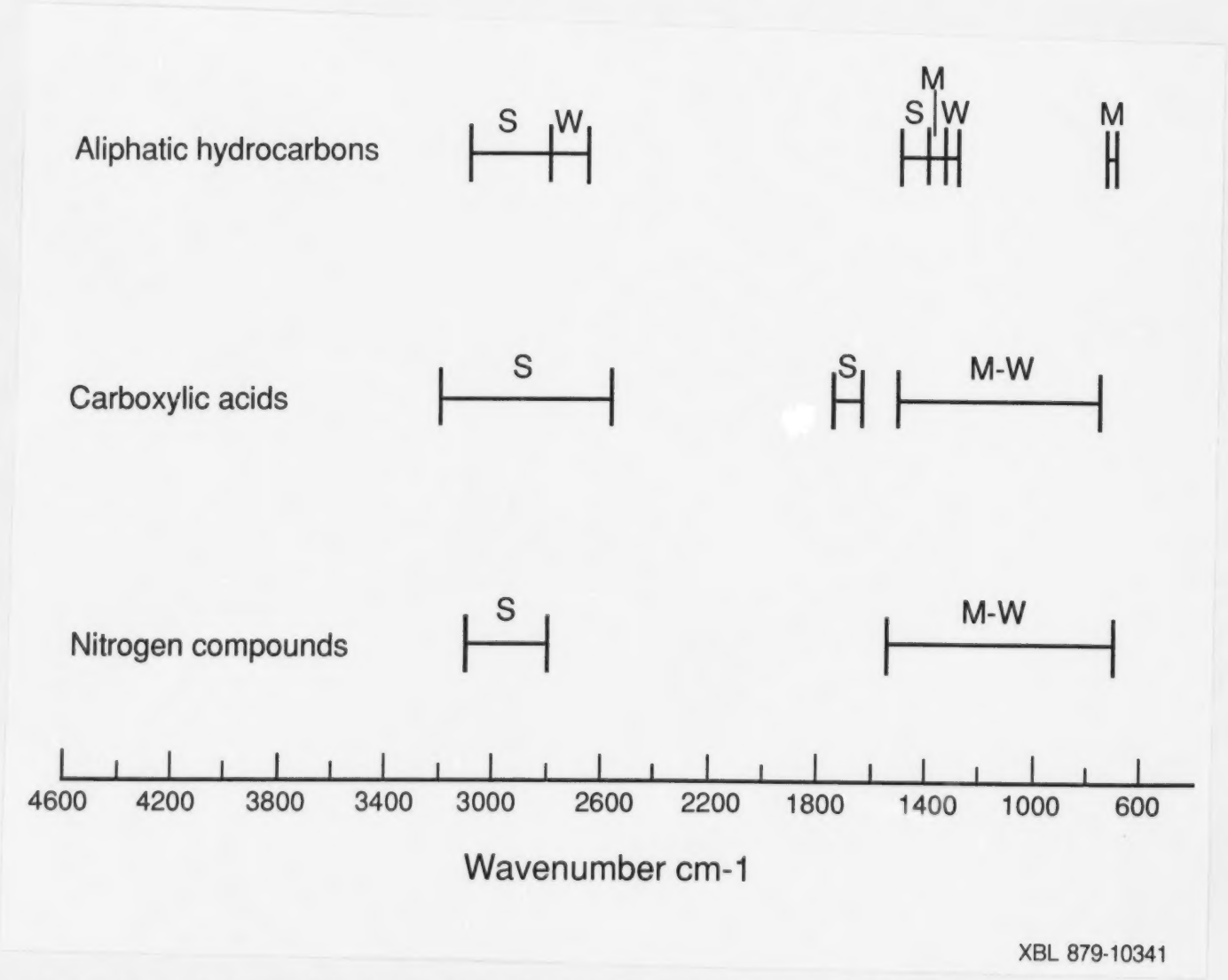

Fig. 6-6. Regions of absorption due to some classes of organic compounds found in ambient aerosols.

1. It is unlikely that organic compounds will absorb significantly in this region of the infrared spectrum.
2. There are no interfering absorbance bands due to Teflon*, sulfate, or nitrate in this region of the spectrum.
3. This region is near the 514 cm^{-1} Teflon* band used as a reference for background subtraction. The absorbance values of the background subtracted spectra will be most valid near the Teflon* reference band.
4. Scattering for 0.1 μm particles, a typical diameter for ambient particles, is insignificant at this wavelength. Mie scattering calculations in our laboratory and elsewhere (Jennings, 1978; Roessler, 1982) have shown that the scattering efficiency for particles less than 1 μm in diameter for wavelengths greater than 11 μm (less than 900 cm^{-1}) is near zero.

The 65 quartz filters were analyzed for organic and elemental carbon. The 30 Teflon* filters were analyzed for elemental carbon. The aerosols were collected on these filters using three air samplers (samplers 1, 2, and 3) each of which sampled fine fraction particles in two intake channels (channels A and B). Table 2 shows the results of the analysis of each filter in each channel of each sampler, the sampled air volume in cubic meters, and the date and time of sampling. The sampling times nominally correspond to a 0800 - 2000 and 2000 - 0800 sampling schedule. Two sets of FTIR results are shown reflecting the two independent calibration procedures as discussed below.

We can compare the results of the thermal and optical methods by plotting the average value of each method during each sampling interval. Figure 6-7 is a plot of the daily average measured area in the 650-666 cm^{-1} region of the background corrected infrared spectra of the ambient aerosols versus the average elemental carbon results measured by the thermal method on the quartz filters. It can be seen that the results are highly correlated (N = 16, r = 0.90) except for the one measurement during sampling period 3-7 which has an excessively high integrated absorbance area. This measurement has

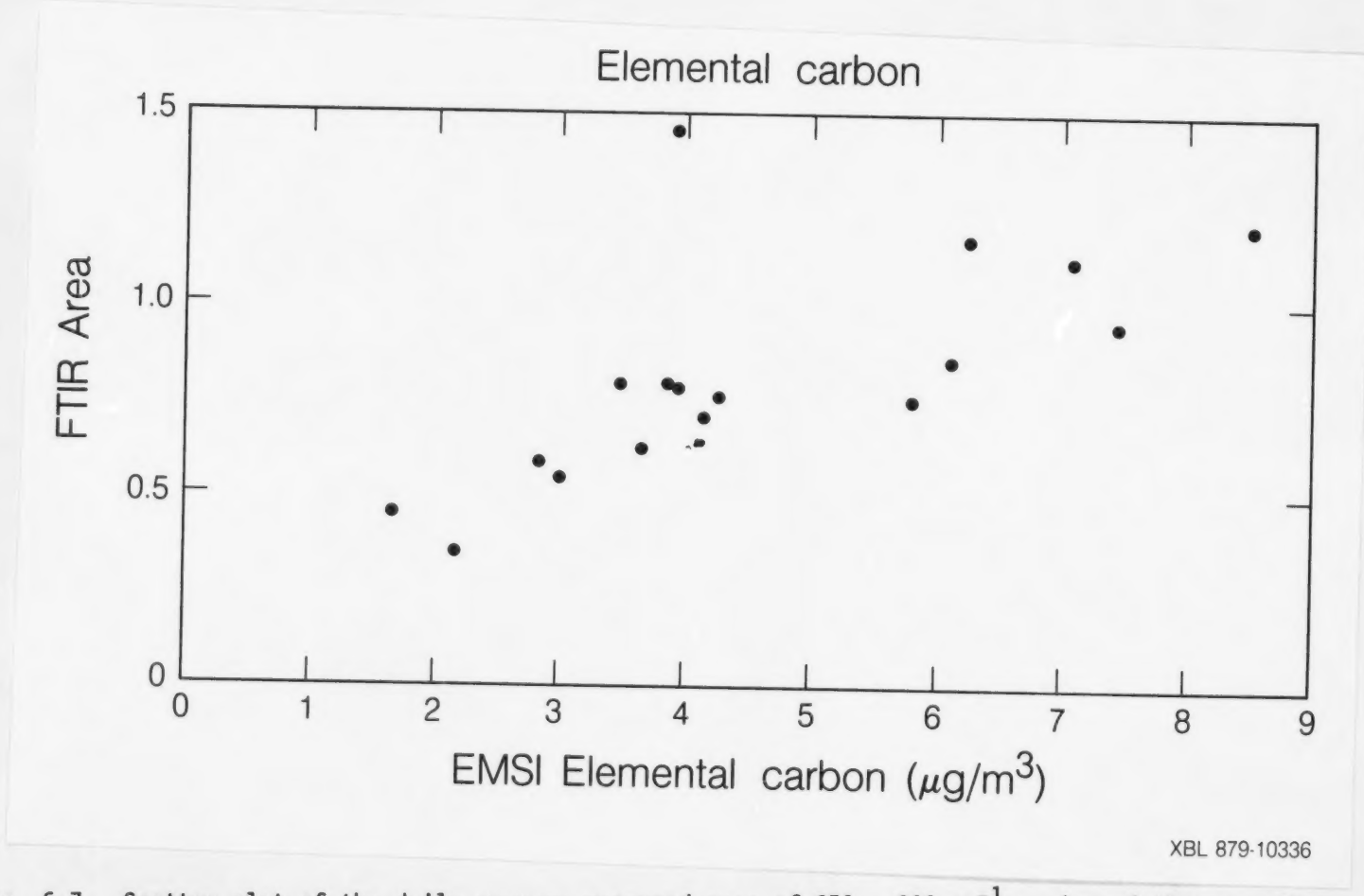

Fig. 6-7. Scatter plot of the daily average measured area of 650 - 666 cm^{-1} region of the aerosol spectra versus the daily average ambient carbon concentration determined by thermal carbon analysis.

been considered an outlier for all subsequent linear regression calculations but has been included in the table and figures. This measurement is high relative to the other measurements as if it were contaminated by additional carbon material. Sulfate measurements on this same filter did not show it to be an outlier for sulfate analysis. It was also found to be an outlier relative to carbon measurements made by other participants in the CARB study.

Another way to analyze the data in Table 2 is to compare the results based on paired quartz and Teflon* filters from the same sampler for each sampling interval. There were 23 pairs of filters that can be compared in this manner. This comparison can be considered to be a calibration of the FTIR technique using the results of the carbon thermal analysis as a standard reference method. A linear least squares fit line was calculated for this data (slope = 0.1042, intercept = 0.2762, N = 23, r = 0.870). The measured FTIR elemental carbon particle concentration during the CARB study using this calibration is shown in the second to last column of Table 2. With this calibration procedure it is not surprising that the FTIR measurements agree with the EMSI thermal analysis. Figure 6-8 shows the results of LBL and two other participants in the CARB study compared to the elemental carbon measured by EMSI. Hansen's (1984) real time measurements were made by an aethalometer. Appel's measurements were made by laser absorption on quartz filters. There is good agreement for elemental carbon measured by all the participants shown in Figure 6-8.

An independent calibration was made using soot standards prepared in the laboratory. Propane soot was deposited on Teflon* filters so that the range of blackening of the filters corresponded to the range observed on the CARB samples. Gravimetric analysis showed that the soot mass loading on the standards were comparable to ambient soot mass loadings on the ambient sample filters. A linear least squares calibration equation relating measured spectral area to propane soot mass concentration was calculated (slope = 0.0268, intercept = 0.0166, N = 8, r = 0.984). The ambient FTIR measured elemental carbon concentration during the CARB study based on this calibration is shown in last column of Table 2.

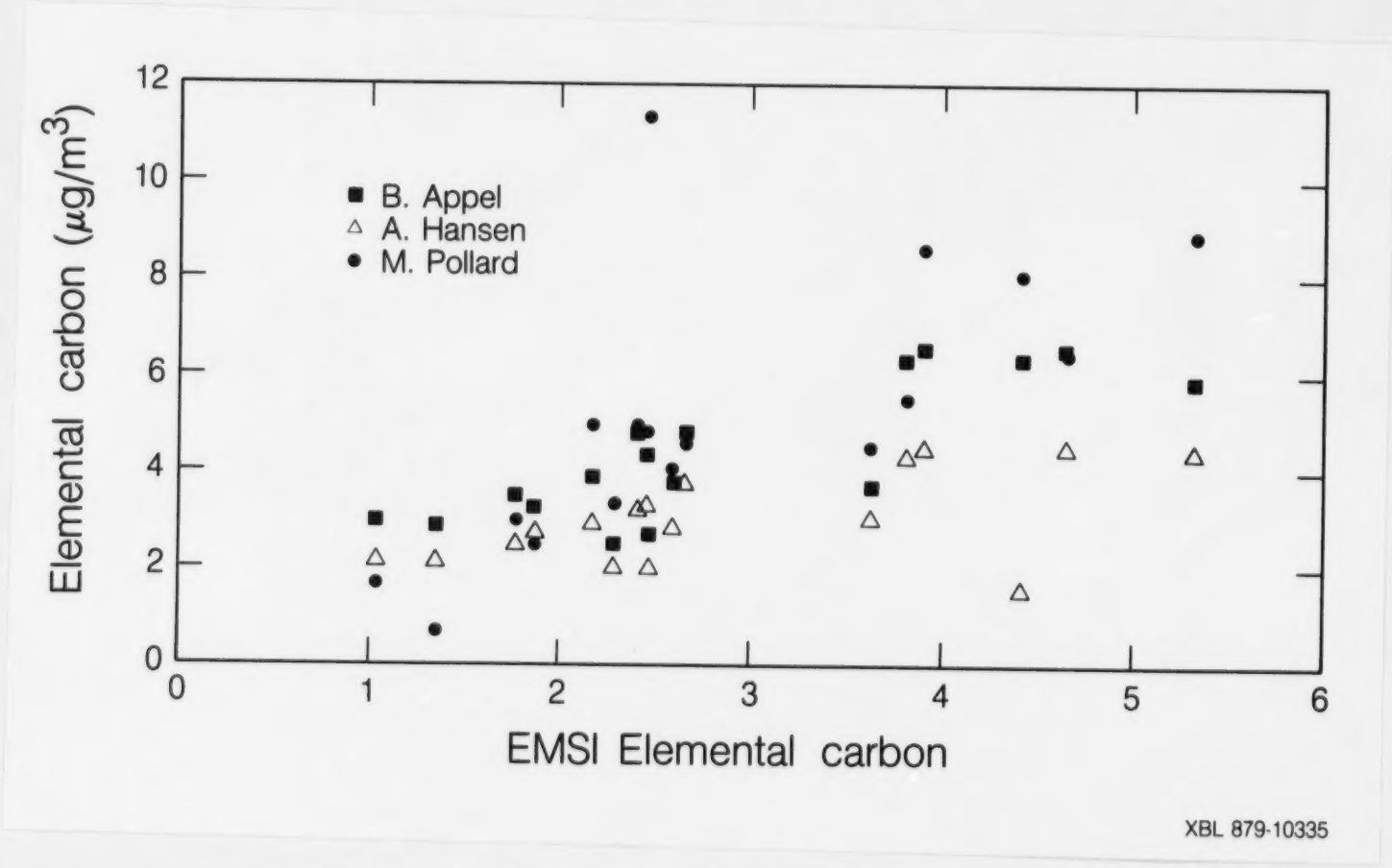

Fig. 6-8. Average ambient carbon concentrations determined by B. Appel, A. Hansen, and M. Pollard versus the elemental carbon concentration determined by EMSI during 12-hour sampling periods.

The ambient elemental soot concentrations calculated from the calibration computed from the absorbance measurements of the propane soot standards are consistently higher than the results calculated from the calibration computed from the results of the thermal methods. This indicates that there is much less absorption for a given mass concentration of propane soot than for the same mass concentration due to ambient soot. This can be seen by comparing the FTIR results in the last two columns of Table 2. One possible source of error could be that the carbon standards were too heavy due to adsorbed water on the particles or the presence of organic compounds. Although the absorption bands of these compounds could not be detected in the infrared spectra of the carbon standards, they could still contribute to some error in the gravimetric analysis of the standards.

Electron micrographs show significant morphological differences between the propane soot and ambient particles. The propane soot is present as long thin agglomerated filaments whereas ambient particles are present as larger diameter granular particles. These morphological dissimilarities and the different optical cross sections of these particles may also contribute to the observed differences in the results shown in Table 2.

Another significant difference between the propane soot standards and ambient samples is that ambient samples are a mixture of absorbing (carbon) and nonabsorbing (ammonium sulfate, ammonium nitrate) particles. Previous authors (Ackerman and Toon, 1981; Bennett and Patty, 1982; Clarke, 1982) have determined that mixtures of carbon and ammonium sulfate have different absorption properties than the pure components alone. In addition, the embedding of small particles deep in the fibrous Teflon* filter would increase absorption due the multiple scattering within the filter. We conclude that there are a number of questions that require further investigation before calibration against a direct carbon standard can succeed. However, calibration is feasible using thermal combustion analysis of co-collected samples on quartz filters. The thermal combustion analysis can be related to chemical and gravimetric analysis of carbon standards.

Conclusions

The primary conclusion resulting from this study is that there is a high correlation between the integrated area of selected portions of the infrared spectrum of ambient aerosols and carbon measured by current thermal methods. The spectral regions selected for integration can be chosen to avoid regions of significant organic absorbance and in fact correlate more highly with measurements of elemental carbon than with organic carbon. It is possible to quantitatively determine carbon concentrations on the filter using a suitable calibration method.

At the present time, calibrations must be made by collecting quartz filter samples in parallel with Teflon* filters and analyzing the quartz filters by thermal methods. An independent calibration based on propane soot standards proved to be unsatisfactory. No definitive reasons could be determined why this method of calibration doesn't agree with thermal methods except to note that the propane soot particles exhibited significant morphological differences relative to ambient particles and that they were not present as a mixture with nonabsorbing particles as is the case for ambient particle samples.

SECTION 7

QUANTITATIVE ANALYSIS OF AMMONIUM NITRATE

INTRODUCTION

Ammonium nitrate is one of the major particulate chemical species found in ambient aerosols. During the Carbonaceous Species Methods Intercomparison (CARB) Study, high concentrations of nitrate compounds were visually detected in the infrared spectra of five filter samples collected during three sampling intervals. Low nitrate concentrations were detected during three other sampling intervals. The nitrate absorption band in Figure 6-1 corresponds to a high filter concentration of nitrate. Low concentrations are observed to be smaller shoulders on the ammonium band. Ion chromatography analysis of the same filters for nitrate confirmed these visual observations of the infrared spectra.

Quantitative infrared analysis of ammonium nitrate requires distinctly different procedures than those developed for the analysis of ammonium sulfate. The difference in the analysis is the result of the severe overlap of the ammonium absorption band with the nitrate absorption band. In addition, the ammonium absorption band from ammonium sulfate interferes with the ammonium and nitrate absorption bands of ammonium nitrate. A comparison of the ammonium sulfate and ammonium nitrate spectra in Figures 4-3 and 4-4 demonstrates the spectral band interference. The background subtraction techniques used to remove the interference of the Teflon* absorbance bands from the ammonium sulfate absorbance bands will not work in the case of ammonium nitrate in ambient particulate samples because the ammonium, nitrate, and sulfate ions are deposited simultaneously. Any quantitative analysis method must take into account the presence of both of these compounds.

McClenny, et al. (1985) reported quantitative results for the analysis of archived air samples for ammonium cation. There was no ammonium nitrate on their filters to interfere with the ammonium analysis. Ammonium nitrate is volatile at ambient temperatures (Stelson, 1979). It is likely that any ammonium nitrate that may have been on the filters volatilized during storage. Volatilization of ammonium nitrate is a significant problem even for fresh air samples. Ammonium nitrate has been shown to volatilize during air sampling (Appel, 1980, 1984). Any ammonium nitrate remaining on the filter is due to the particles collected during the latter portion of the sampling interval. All of the high ambient nitrate concentrations reported in the CARB study occurred during the hours of 2000 - 0800 when cooler nighttime temperatures favored the formation of solid phase ammonium nitrate and retarded volatilization from the filters during sampling.

A method for quantitatively determining ammonium nitrate in the presence of ammonium sulfate will be presented in this section.

EXPERIMENTAL PROCEDURES

Laboratory Test Aerosol Samples

Twelve aerosol samples, containing both ammonium nitrate and ammonium sulfate, were prepared. The particles were generated with the aerosol generator and deposited on the filters in the fine fraction channel of a dichotomous sampler. Concentrated (0.2 M) solutions of ammonium nitrate and ammonium sulfate were sequentially aspirated into the aerosol generator. The high aerosol concentrations allowed the sampling time to be reduced to prevent any possibility of revolatilization of the ammonium nitrate into the filtered air stream. The longest sampling time for any filter was 130 seconds.

Reference spectra of the blank filters were measured prior to particle deposition. Ammonium nitrate was deposited on the filters first. Samples were collected for six different time intervals resulting in six different filter concentrations. Spectra of the filters were measured immediately after ammonium nitrate deposition. Ammonium sulfate was then deposited on the filters in two different concentrations. The filters were prepared so

that there would be a high and low concentration of ammonium sulfate for each of the six concentrations of ammonium nitrate. Spectra of the filters were measured again after deposition of ammonium sulfate.

Absorbance Band Model for the Ammonium Absorption of Ammonium Sulfate

The absorption spectrum of ammonium sulfate has an ammonium absorbance band located at 1420 cm^{-1} (Figure 4-3). This band severely overlaps the ammonium and nitrate absorbance bands shown in Figure 4-4. Typical ambient air samples will contain both ammonium sulfate and ammonium nitrate. Integration of the absorbance spectrum between 1320 - 1560 cm^{-1} will include the absorbance due to ammonium nitrate and the ammonium band due to ammonium sulfate. In order to determine the concentration of ammonium nitrate, the concentration of ammonium due to ammonium sulfate must also be calculated.

The sulfate concentration on the filters is determined from a measurement of the area of the sulfate absorbance band in the 595 - 635 cm^{-1} region of the spectrum. If we make the assumption that all of the sulfate is due to ammonium sulfate, we can not only calculate the amount of ammonium due to the ammonium sulfate but also the shape of the ammonium absorption band. This is done by determining a function that will reproduce the ammonium absorbance band shape from a measurement of the sulfate concentration.

This function was determined by modeling the ammonium band in each of the spectra of a set of ammonium sulfate calibration standards. The ammonium band spectra were baseline corrected prior to the modeling calculations. The shape of an infrared absorbance band of materials in the condensed phase is given to a good approximation by a Lorentzian function (Griffiths, 1986). The shape of the ammonium band in the ammonium sulfate spectrum suggests that two overlapping Lorentzian bands would more accurately model the ammonium spectrum. The choice of two Lorentzian bands is arbitrary and is not based on any analysis of the ammonium vibrational transitions in this energy region. The least squares fit of the following function in six parameters:

$$\frac{Q_1}{1 + [Q_2 \cdot (\nu - Q_3)]^2} + \frac{Q_4}{1 + [Q_5 \cdot (\nu - Q_6)]^2}$$

was calculated for the ammonium band (1335 - 1550 cm^{-1}) in each ammonium sulfate calibration standard where:

Q_1, Q_4 = peak heights of the two Lorentzian functions

Q_2, Q_5 = 1/(half width at half height)

Q_3, Q_6 = band position

ν = wavenumbers

The parameters Q_2, Q_3, Q_5, and Q_6 are constants for the ammonium band of ammonium sulfate. Q_1 and Q_4 are proportional to the concentration of ammonium and therefore can be calculated from the measured concentration of sulfate.

The parameters Q_2, Q_3, Q_5, and Q_6 were averaged for all of the calibration spectra to produce the following values:

Q_2 = 0.0649 ± 0.0031
Q_3 = 1422.29 ± 0.35
Q_5 = 0.0506 ± 0.0023
Q_6 = 1449.22 ± 0.56

Q_1 is calculated from the sulfate area from the equation: Q_1 = 0.0814* (SO_4 area at 620 cm^{-1}) - 0.0024. Q_4 can be calculated from the equation: Q_4 = 0.5230*Q_1 + 0.0026.

RESULTS AND DISCUSSION

Laboratory Experiment

The constant parameters Q_2, Q_3, Q_5, and Q_6 are extremely uniform over a wide range of ammonium sulfate filter concentrations (7 - 86 $\mu g/cm^2$). Figures 7-1 and 7-2 are plots of the calculated ammonium absorption band shape and the actual ammonium band absorption data for high (44.8 $\mu g/cm^2$) and low (5.6 $\mu g/cm^2$)concentrations of ammonium sulfate. The parameters Q_1 and Q_4

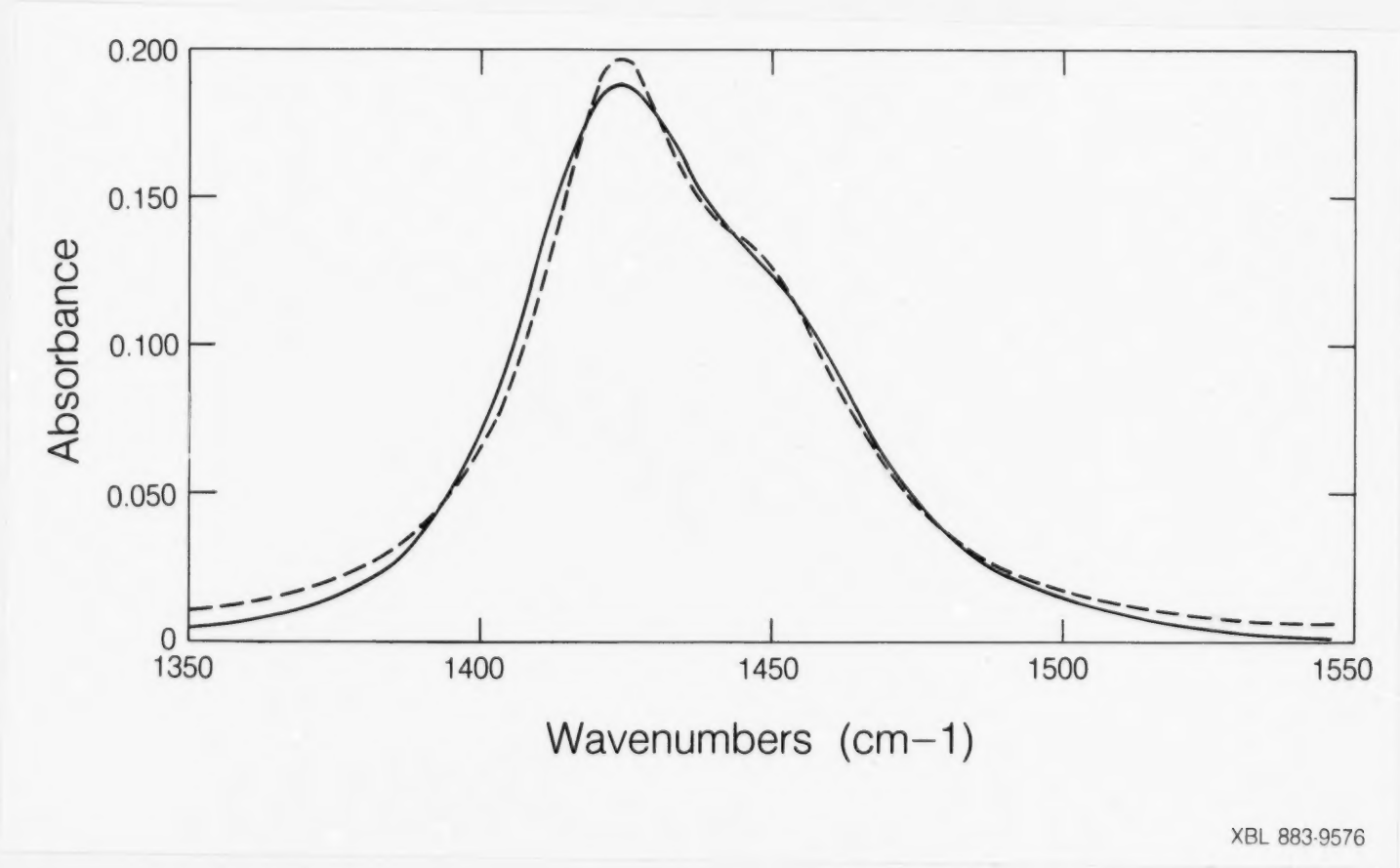

Fig. 7-1. Ammonium band absorption data and calculated ammonium band shape (44 μg/cm^2). The solid line is the measured data. The dashed line is the calculated data.

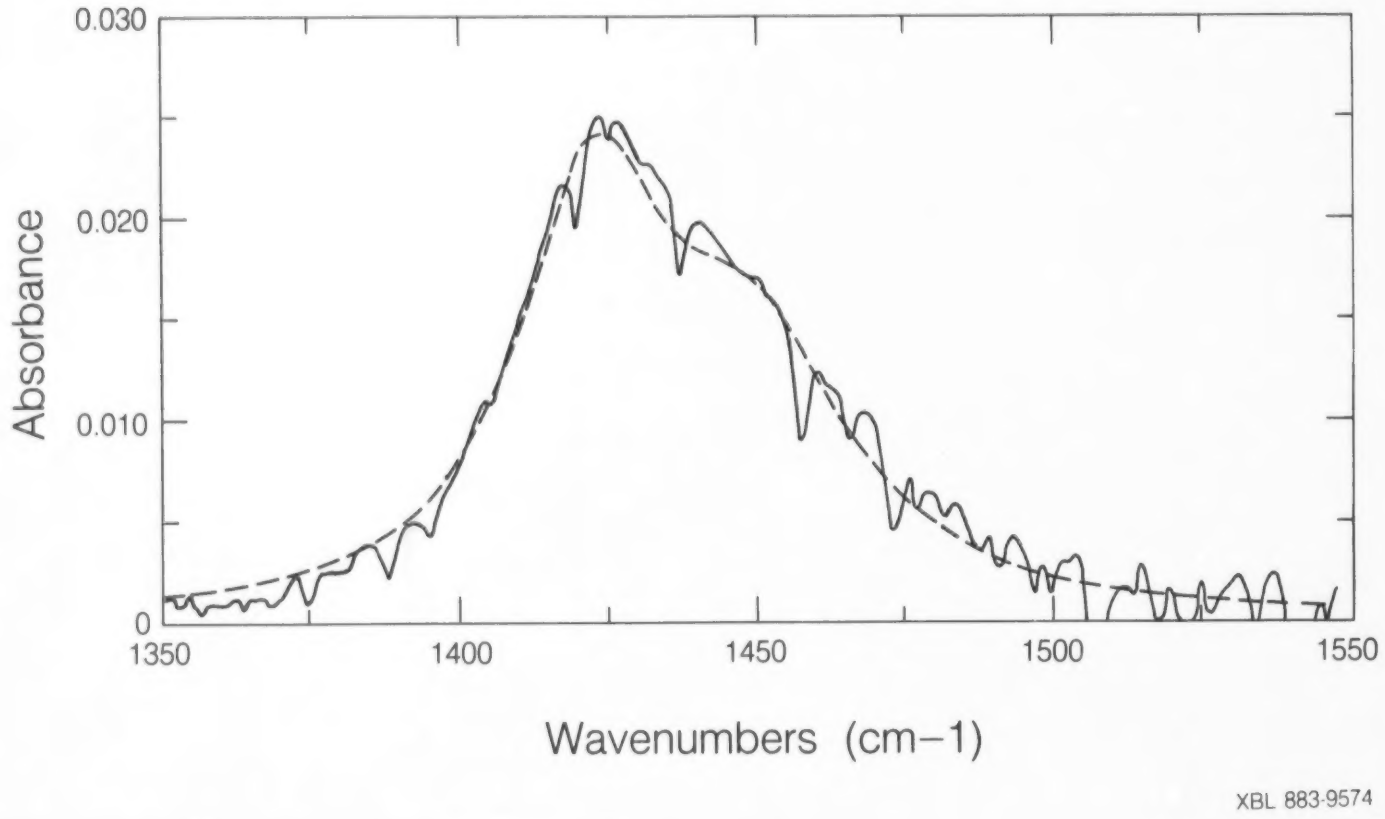

Fig. 7-2. Ammonium band absorption data and calculated ammonium band shape (5.6 $\mu g/cm^2$). The solid line is the measured data. The dashed line is the calculated data.

were calculated from the area of the sulfate absorption band at 620 cm^{-1}. Note the absorbance scale difference in each figure.

The calculation of the concentration of ammonium nitrate in the presence of ammonium sulfate is now straightforward. First, the area of the sulfate band at 620 cm^{-1} is measured. The parameters Q_1 and Q_4 are then determined and the calculated ammonium band spectrum is subtracted point by point from the filter spectrum in the 1320 - 1560 cm^{-1} region. The remaining absorbance is due to ammonium nitrate. The ammonium nitrate calculated with this method can be compared to the ammonium nitrate calculated from the set of spectra measured before the deposition of ammonium sulfate. The results are shown in Table 3. The ammonium nitrate measurements were the same to within 3 - 5%.

The detection limit (3σ) for the determination of ammonium nitrate in the presence of ammonium sulfate is 1.32 $\mu g/cm^2$. This detection limit is calculated from standard spectra of laboratory generated aerosol samples. It is expected that the detection limit will be somewhat higher for the analysis of ambient samples because of the increased uncertainty of drawing an appropriate baseline under the ammonium nitrate absorption band. The nitrate and sulfate filter concentrations of the samples shown in Table 3 are comparable to the nitrate and sulfate concentrations measured on sample filters collected during the CARB study. There is a small but predominant increase in the measured ammonium nitrate after the deposition of ammonium sulfate. The cause of this bias is unknown. There is no indication that the detection limit is dependent on the sulfate concentration. It would be expected that the detection limit for ammonium nitrate would increase with higher relative sulfate concentration than those shown in Table 3.

Success with ambient samples will require that the filter orientation be maintained throughout the analysis to obtain the best subtraction of the Teflon* substrate. In addition, a large data base of ambient spectra with deposits of ammonium sulfate, ammonium nitrate, and carbon particles is required to develop an empirical method of drawing an accurate baseline under the ammonium nitrate absorption band.

TABLE 3. Comparison of ammonium nitrate measurement before and after deposition of ammonium sulfate.

Filter	Ammonium Nitrate $\mu g/cm^2$ Before Ammonium Sulfate Deposition	Ammonium Nitrate $\mu g/cm^2$ After Ammonium Sulfate Deposition	% Difference	Ammonium Sulfate $\mu g/cm^2$
1	21.915	22.733	3.73	19.906
2	23.221	23.747	2.27	39.563
3	25.534	26.253	2.82	19.585
4	26.522	26.709	0.71	39.694
5	30.613	31.242	2.05	20.169
6	29.684	30.075	1.32	40.391
7	18.434	19.267	4.52	18.141
8	17.831	18.122	1.63	36.571
9	15.040	14.895	-0.96	18.680
10	14.144	14.505	2.55	32.260
11	12.375	11.648	-5.87	19.451
12	11.240	11.313	0.65	35.963

SECTION 8

CHEMICAL INTERACTIONS ON FILTERS

GENERAL INTRODUCTION

Fourier transform infrared spectroscopy is sensitive to the chemical form of the analyzed species. There are significant spectral differences between different sulfate species and different nitrate species. It is therefore important to understand the chemical reactions that can occur between the particles collected on the filter because the resulting products can alter the infrared spectra. There is a large increase in particle density when a cubic meter of air is passed through a filter with a 32 cm^2 area. In addition, water vapor and water droplets are concentrated on the hydrophobic Teflon* material. For a sufficiently high particle density this is a favorable environment for artifacts associated with particle/particle and gas/particle interaction. The FTIR spectrometer is an ideal instrument with which to investigate these interactions.

AMMONIUM NITRATE/AMMONIUM SULFATE FILTER CHEMISTRY

Introduction

Examination of the spectra of ammonium nitrate and ammonium sulfate measured during the CARB study revealed features which had not been observed in the spectra of the respective laboratory-generated compounds. One observation is a shift in the position of the sulfate band at 1117 cm^{-1} to 1090 ± 6 cm^{-1} in the CARB spectra. This is a significant change in the band position. Instrumental error is ruled out because the location of the Teflon* band at 1151 cm^{-1} has not changed. The nitrate band at 1371 cm^{-1} has also shifted to 1340 cm^{-1} in the CARB spectra. Finally the nitrate band at 832 cm^{-1} is split into two distinct bands at 832 cm^{-1} and 825 cm^{-1}.

Although the spectra of the CARB samples showed shifts in the position of the absorption bands, the spectra were qualitatively similar to the ammonium sulfate and ammonium nitrate spectra generated in the laboratory. The CARB spectra were therefore analyzed as if the absorbance bands were due to ammonium sulfate and ammonium nitrate. The results of the ion chromatography (IC) analysis for sulfate on the filters is consistent with the interpretation that the absorption band is due to sulfate. There is excellent agreement between the integrated area of the 620 cm^{-1} sulfate band and the sulfate measured by IC.

The change in the band positions could be due to the presence of nitrate and sulfate in a chemical form other than ammonium sulfate and ammonium nitrate. This could produce small shifts in the infrared absorption without significantly affecting the strength of the absorption. In order to investigate this hypothesis, the compounds $2NH_4NO_3.(NH_4)_2SO_4$ (2:1 mixed salt), and $3NH_4NO_3.(NH_4)_2SO_4$ (3:1 mixed salt) were studied as the possible forms of ammonium, sulfate, and nitrate measured in the CARB study samples.

Experimental Procedures

Particulate samples of the three compounds $2NH_4NO_3.(NH_4)_2SO_4$, and $3NH_4NO_3.(NH_4)_2SO_4$ were deposited on Teflon* filters. The 2:1 and 3:1 mixed salts of ammonium nitrate and ammonium sulfate were prepared from the appropriate stoichiometric mixtures of ammonium nitrate and ammonium sulfate in water. The chemical form and purity of the mixed salts was confirmed with x-ray diffraction measurements of the filters.

Results

Figure 8-1 is a infrared spectrum of $2NH_4NO_3.(NH_4)_2SO_4$. Figure 8-2 is a spectrum of $3NH_4NO_3.(NH_4)_2SO_4$. The locations of the ammonium absorption band at 1425 cm^{-1}, the nitrate band at 1340 cm^{-1}, and the sulfate bands at 1117 cm^{-1} and 1081 cm^{-1} are identical for both the 2:1 mixed salt and the 3:1 mixed salt. The relative peak heights of the nitrate bands at 832 cm^{-1} and 825 cm^{-1} are different for each salt. Finally, the sulfate bands for each salt in the 620 cm^{-1} region are at slightly differently locations (622 cm^{-1}

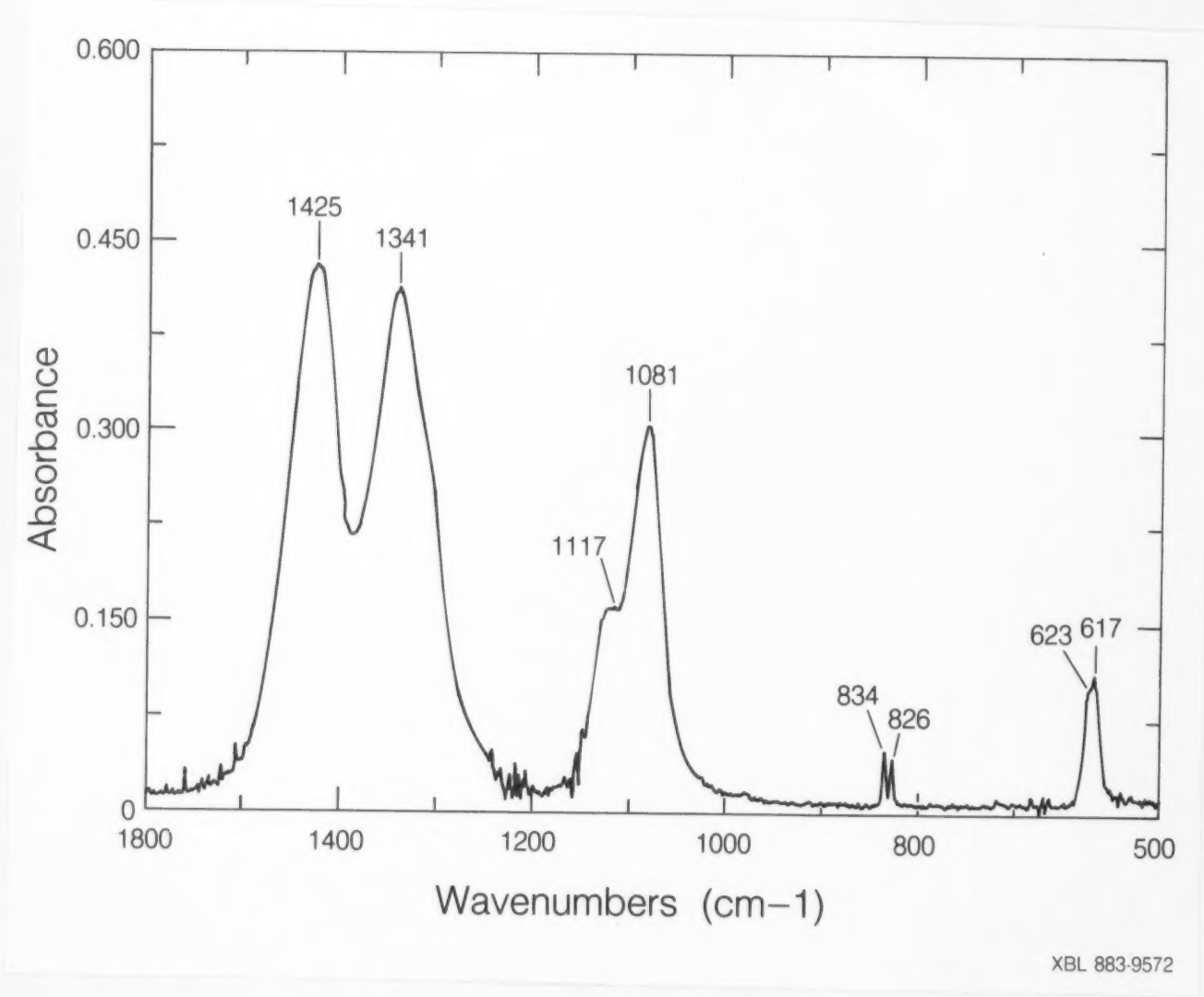

Fig. 8-1. 2 $NH_4NO_3 \cdot (NH_4)_2SO_4$ spectrum.

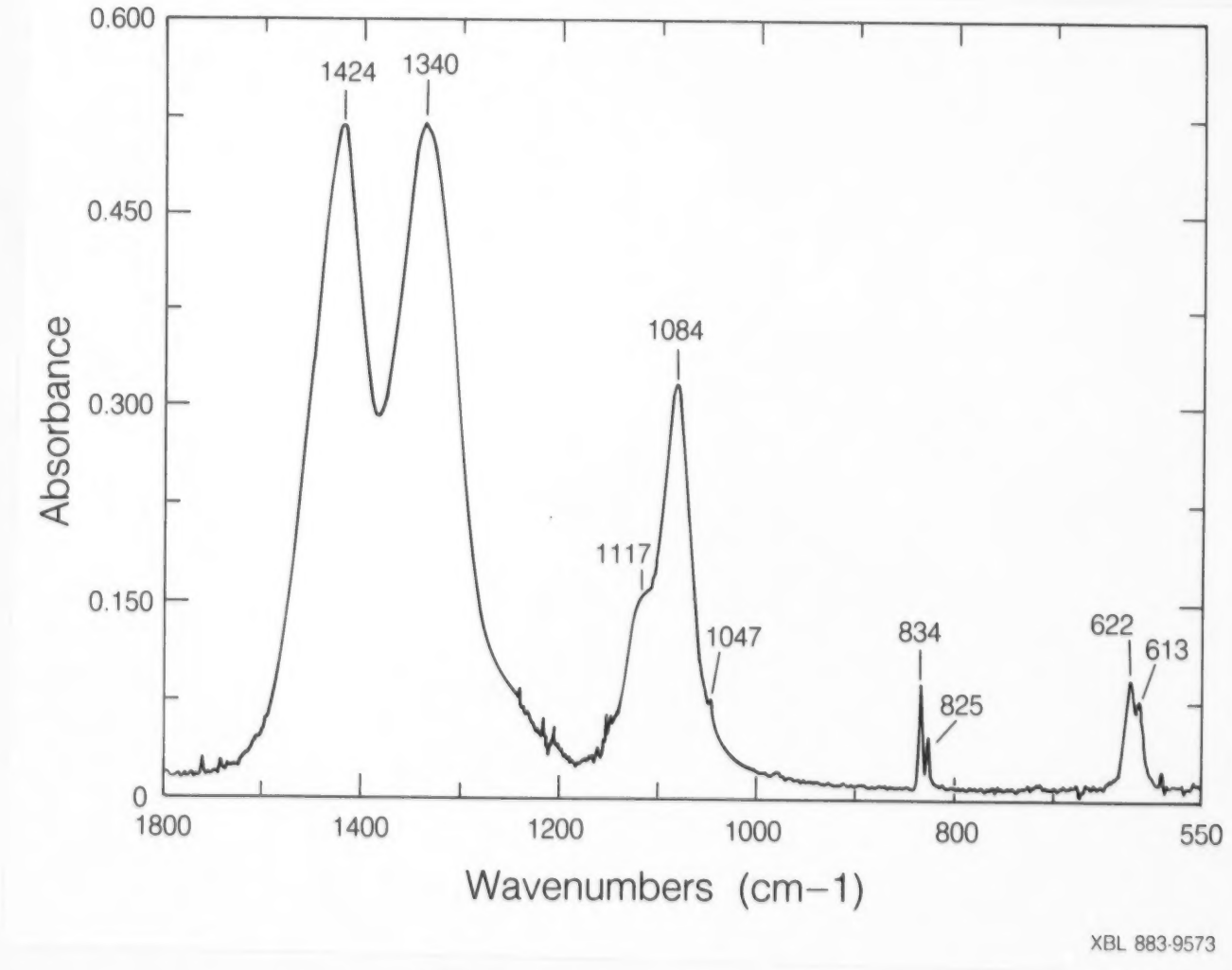

Fig. 8-2. $3NH_4NO_3 \cdot (NH_4)_2SO_4$ spectrum.

and 617 cm^{-1} versus 622 cm^{-1} and 617 cm^{-1}) and have different relative peak heights. The sulfate and nitrate band positions in Figures 8-1 and 8-2 are identical to the band positions measured in the CARB spectra in Figure 6-1. The split band present in the mixed salt spectra is also present in the CARB spectra. One difference between the mixed salt spectra and the CARB spectra is that the sulfate band at 620 cm^{-1} is not split in the CARB spectra. The similarity of the 2:1 and 3:1 mixed salt spectra makes it difficult to determine which mixed salt is present in the ambient samples or whether there is a combination of the two salts.

Discussion

A number of papers in the literature reporting x-ray diffraction experiments on ambient filters confirm the presence of the mixed salts $2NH_4NO_3 \cdot (NH_4)_2SO_4$ and $3NH_4NO_3 \cdot (NH_4)_2SO_4$ (Tani, et al., 1983; Harrison, 1984). Recent papers by Basset (1983, 1984) and Pilinis (1987) show that chemical models of the Los Angeles air basin, the location of the CARB study, predict the formation of significant quantities of these mixed salts during the summer months.

The presence of the mixed salts on the CARB study filters poses the question as to whether the mixed salts were formed in the atmosphere prior to collection on the filters or whether they were formed on the filter as a result of chemical interactions of ammonium nitrate and ammonium sulfate particles. This was studied by loading a filter with high concentrations of ammonium nitrate and ammonium sulfate. The concentrations were purposely made high to ensure that there would be particle/particle contact. The relative humidity was < 1% during deposition of the particles. An infrared spectra was measured immediately after particle deposition. The result was a filter with a spectrum in which the nitrate band shifted from 1340 cm^{-1} to 1314 cm^{-1} and the sulfate band shifted from 1117 cm^{-1} to 1078 cm^{-1}. The nitrate band at 832 cm^{-1} split into two bands located at 833 and 828 cm^{-1}. X-ray diffraction measurements of this filter showed the presence of the 3:1 and the 2:1 salts along with excess ammonium nitrate and a trace of ammonium sulfate. This demonstrates that not only do ammonium nitrate and ammonium sulfate interact on the filter but that they can do so under very dry ambient conditions.

The mixed salts of ammonium nitrate and ammonium sulfate can be predicted from the thermodynamics of the NH_3-HNO_3-H_2SO_4-H_2O system (Tang, 1981; Stelson, 1982). The formation of the 3:1 and the 2:1 salts on the filter substrate most likely depends on the local stoichiometry conditions seen by each particle. Scanning electron micrographs of this filter showed the presence of particles on the order of 20 μm in diameter in contrast to the smaller particles (< 2.5 μm diameter) deposited with the dichotomous sampler. Apparently the ammonium nitrate and ammonium sulfate particles fused into larger particles of the mixed salts.

Ammonium nitrate and ammonium sulfate will interact at lower filter concentrations in the presence of high relative humidity air. A filter was prepared with ammonium nitrate and ammonium sulfate in concentrations comparable to the higher concentrations observed during the CARB study. Air at 50% relative humidity was passed through the filter for two hours using the dichotomous air sampler. X-ray diffraction measurements of this filter revealed the presence of the 3:1 mixed salt along with ammonium nitrate and ammonium sulfate. In addition, the diffraction measurement indicated the presence of preferred orientation in the salt crystals. This indicates that the crystals were formed on the filter.

The relative humidity varied between 65 - 100% during the three sampling intervals during the CARB study in which high nitrate levels were observed on the sample filters. It is unknown whether 12 hours of sampling under these conditions could result in complete conversion of the ammonium nitrate and ammonium sulfate to the mixed salts. In the case of extended sampling periods or in the presence of significant quantities of water, these reactions can be expected to occur. It is also likely that the particles were formed in the atmosphere prior to collection. Regardless of where they were formed these salts are not volatile as is ammonium nitrate. They will remain stable on the filters. The presence of these mixed salts should be considered when studying the volatility of nitrate compounds on filters.

AMMONIUM NITRATE/SODIUM CHLORIDE FILTER CHEMISTRY

Introduction

The dissociation, at room temperature, of ammonium nitrate by the reaction:

$$NH_4NO_3\ (s) + \text{air flow} \rightarrow NH_3\ (g) + HNO_3\ (g)$$

has been observed by many investigators (Appel, 1980, 1984; Stelson, 1979). This has led to significant losses of NH_4NO_3 from Teflon* filters during prolonged sampling periods. The loss of NH_4NO_3 has been observed by collecting the evolved HNO_3 (g) on Nylasorb* filters or cellulose filters soaked in Na_2CO_3 or NaCl located after the Teflon* filter. It should also be possible to prevent the loss of ammonium nitrate on the Teflon* filters by depositing a layer of NaCl particles prior to sample collection. The following reaction would be expected to occur:

$$NH_4NO_3\ (s) + NaCl\ (s) \rightarrow NH_4Cl\ (s) + NaNO_3\ (s)$$

Experimental Procedure

NH_4NO_3 and NaCl particles were generated with the laboratory aerosol generator and deposited on 2 μm pore size Teflon* filters. Ambient air samples were collected with a dichotomous sampler in Berkeley, CA.

Results and Discussion

Figure 4-4 is a background subtracted spectrum of ammonium nitrate on a blank Teflon* filter and Figure 8-3 is a spectrum of $NaNO_3$. The nitrate absorption band at 1371 cm^{-1} has shifted to 1405 cm^{-1} in $NaNO_3$. The nitrate band at 832 cm^{-1} has not changed position. NaCl does not absorb infrared radiation nor does NaCl deposited on a Teflon* filters significantly scatter the infrared radiation. The mass concentration of the NaCl particles on the filters was unknown but examination by scanning electron microscopy determined that there was a solid layer of NaCl particles over the entire filter.

NaCl and NH_4NO_3 particles were sequentially deposited on a blank Teflon* filter. Figure 8-4 shows the filter spectrum immediately after deposition of the ammonium nitrate (solid line). The peak of the absorbance band is at 1413 cm^{-1} with a shoulder on the low wavenumber side of the band.

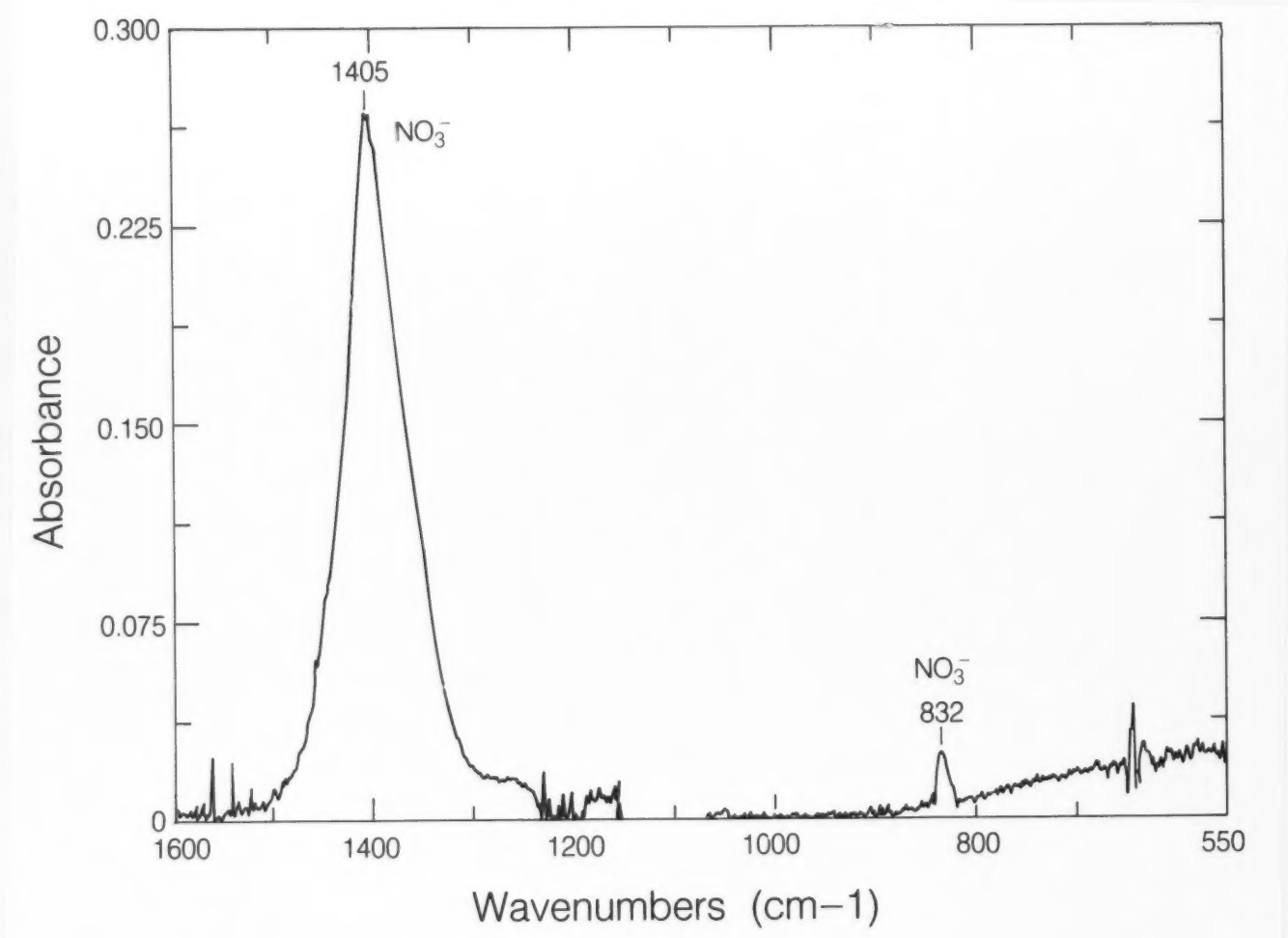

Fig. 8-3. Sodium nitrate spectrum.

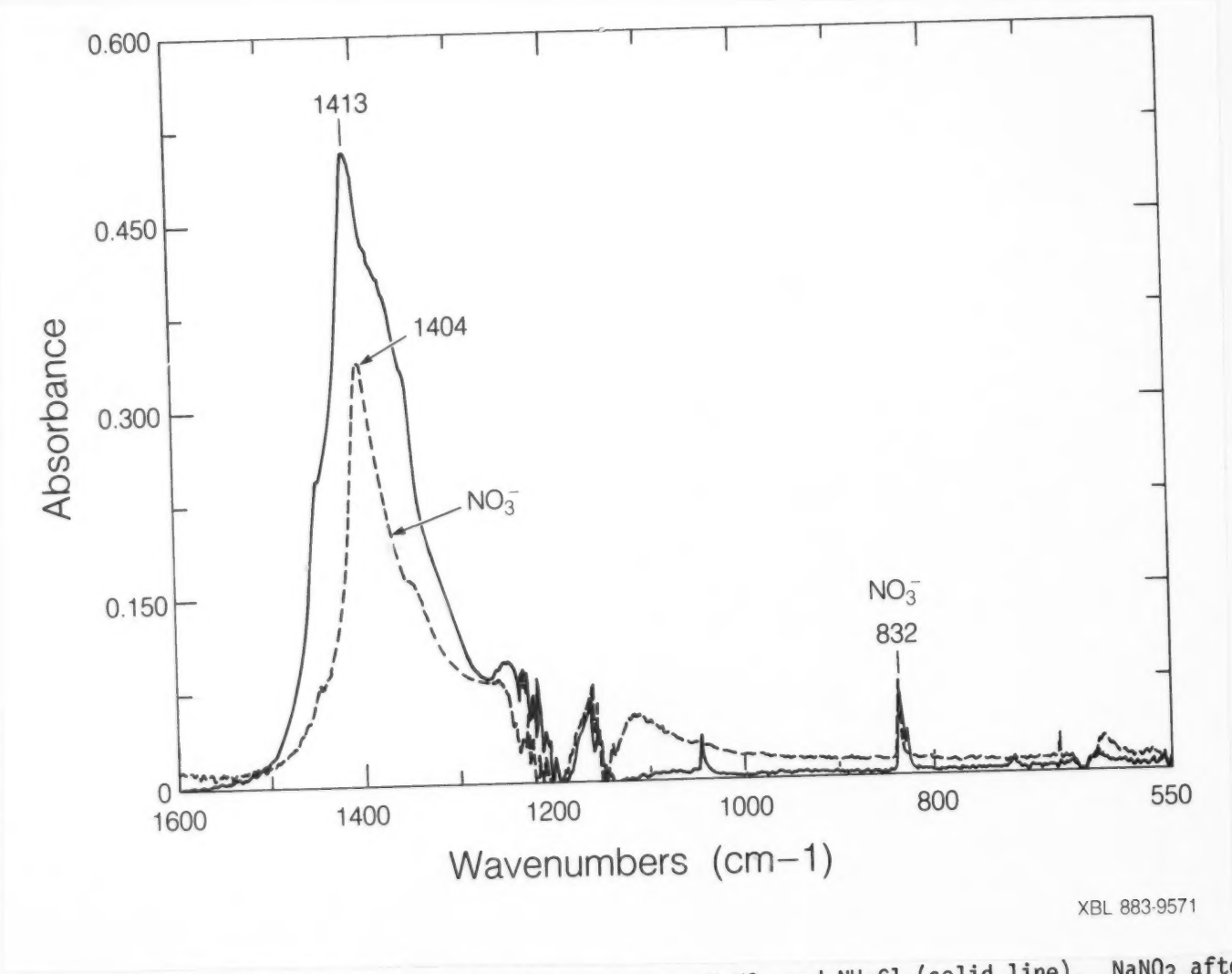

Fig. 8-4. Chemical reaction of NaCl and NH_4NO_3 to form $NaNO_3$ and NH_4Cl (solid line). $NaNO_3$ after volatization of NH_4Cl (dashed line).

This is clearly not an ammonium nitrate spectrum indicating that the ammonium nitrate has chemically reacted with the NaCl upon deposition on the filter. Room air was passed through the filter for 24 hours at a rate of 1 m^3 per hour. The resulting spectrum of the filter is also shown in Figure 8-4 (dashed line). The large band has decreased in height and the peak location has shifted to 1407 cm^{-1}. The small nitrate band at 832 cm^{-1} is the same height indicating that all of the nitrate has remained on the filter.

The loss in the peak height at 1413 cm^{-1} can be explained by volatilization of the NH_4Cl by the reaction: NH_4Cl (s) --> NH_3 (g) + HCl (g). Figure 8-5 is the spectrum of pure ammonium chloride (solid line). Also shown in Figure 8-5 is a spectrum of the NH_4Cl filter after passing room air through it for 24 hours (dashed line). All of the ammonium chloride has been volatilized.

In summary, the sequence of chemical reactions that were observed on the filter for laboratory generated ammonium nitrate and sodium chloride can be written as:

$$NH_4NO_3\ (s) + NaCl\ (s) + \text{air flow} \longrightarrow NH_4Cl\ (s) + NaNO_3\ (s)$$
$$\downarrow$$
$$\downarrow$$
$$\downarrow \longrightarrow NH_3\ (g) + HCl\ (g)$$

An interesting feature of the above reaction is that it appears to occur through direct particle/particle interaction. The conversion of ammonium nitrate to sodium nitrate occurred immediately upon deposition of the particles in < 1% relative humidity air. During ambient air sampling, the above technique would also capture gaseous nitric acid as would the methods utilizing backup filters. Separation of gaseous nitric acid from particulate nitrate during air sampling could be accomplished by stripping the nitric acid from the gas stream with a denuder tube at the entrance to the sampler. No chemical reactions have been observed between $(NH_4)_2SO_4$ and NaCl particles.

An experiment was performed to observe the NH_4NO_3-NaCl reaction during ambient sampling conditions. Two automated dichotomous samplers were

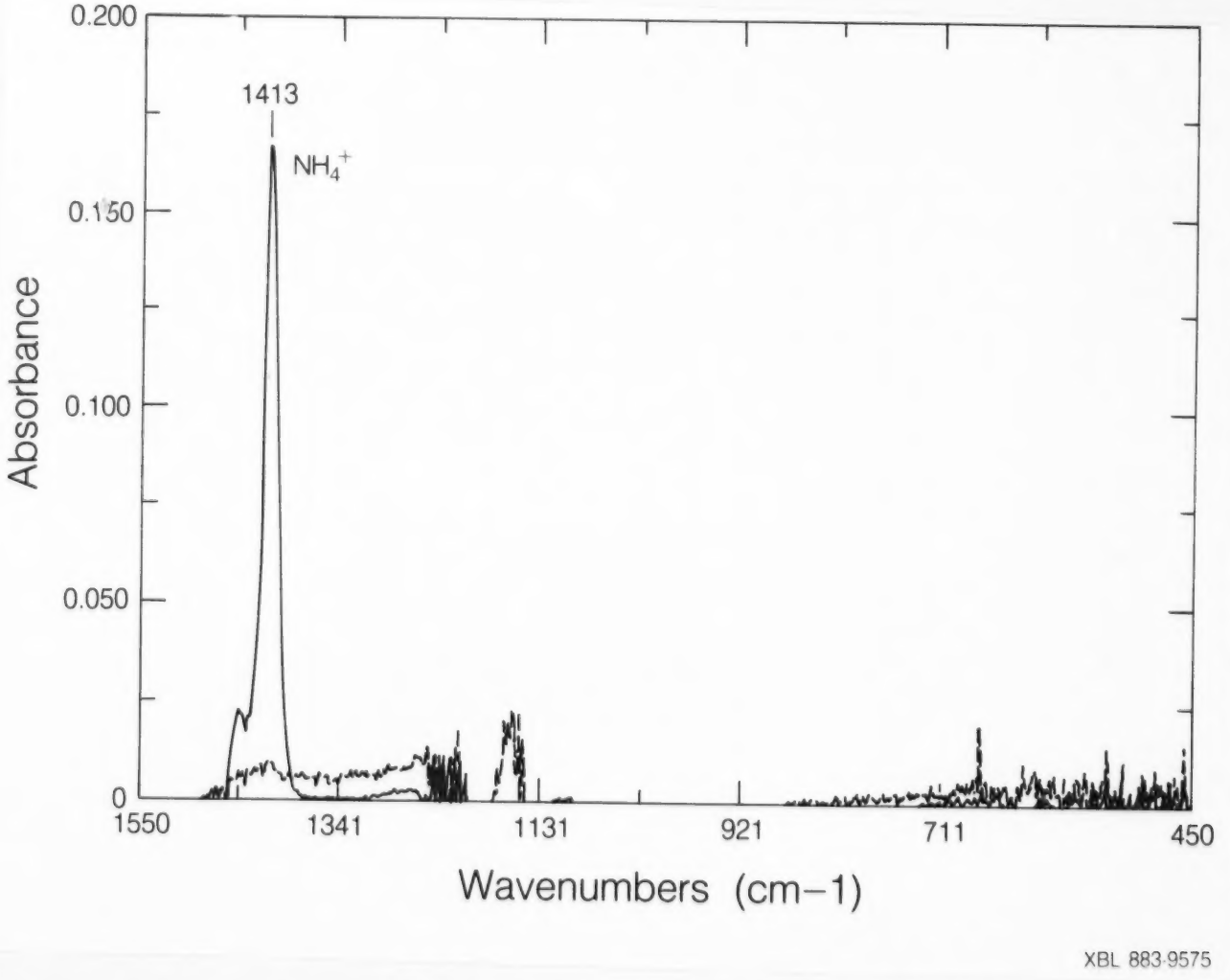

Fig. 8-5. NH_4Cl spectrum (solid line) and removal by volatization (dashed line).

operated in parallel. The flow rates in each sampler were measured to ensure that they were identical (16.7 l/min). A pair of uncoated filters were sampled in parallel for a 24-hour time period. Subsequent FTIR measurements confirmed that the concentration of collected particles was the same on both filters. Next, four pairs of filters were sampled in parallel. The sampling time for each filter pair was 24 hours. Each pair consisted of one uncoated filter and one filter coated with NaCl particles. Each sampler had two coated and two uncoated filters.

After the sampling was completed, FTIR measurements showed that the nitrate levels were approximately the same on all filters. This indicates that either none of the nitrate volatilized from the uncoated filters or that the NH_4NO_3-NaCl reaction was not occurring as it had in the laboratory samples and that there was loss of ammonium nitrate from both filters in each sample pair. More laboratory experiments are required to obtain a better understanding of the chemistry of NH_4NO_3 and NaCl on the filter.

REFERENCES

Ackerman, T. P. and O. B. Toon (1981) Absorption of visible radiation in atmosphere containing mixtures of absorbing and nonabsorbing particles. Appl. Optics 20, 3661-3667.

Akhter, M. S., A. R. Chughtai, and D. M. Smith (1985) The structure of hexane soot I: spectroscopic studies. Appl. Spectros. 39, 143-153.

Aldrich Library of Infrared Spectra, (1978) second edition. (C. J. Pouchert, ed.) Aldrich Chemical Company, Milwaukee, WI.

Appel, B. R., S. M. Wall, Y. Tokiwa, and M. Haik (1980) Simultaneous nitric acid, particulate nitrate and acidity measurements in ambient air. Atmos. Environ. 14, 549-554.

Appel, B. R., Y. Tokiwa, M. Haik, and E. L. Kothny (1984) Artifact particulate sulfate and nitrate formation on filter media. Atmos. Environ. 18, 409-416.

Bassett, M. and J. H. Seinfeld (1983) Atmospheric equilibrium model of sulfate and nitrate aerosols. Atmos. Environ. 17, 2237-2252.

Bassett, M. and J. H. Seinfeld (1984) Atmospheric equilibrium model of sulfate and nitrate aerosols-II. particle size analysis. Atmos. Environ. 18, 1163- 1170.

Bennett, C. A. and R. R. Patty (1982) Monitoring particulate carbon collected on teflon filters: an evaluation of photoacoustic and transmission techniques. Appl. Optics 21, 371-374.

Boone, P. M., J. M. Daisey, and M. J. D. Low (1986) Fourier transform infrared spectroscopy with HPLC to characterize polar particulate matter from the ambient atmosphere. Presented at the Fifth Symposium on Environmental Analytical Chemistry, Atmospheric Chemistry, and Source Apportionment. Brigham Young University, June 18-20.

Cadle, S. H. and P. J. Groblicki (1982) An evaluation of methods for the determination of organic and elemental carbon in particulate samples. In Particulate Carbon: Atmospheric Life Cycle (G. T. Wolff and R. L. Klimisch, eds.) Plenum Press, New York, 89-109.

Clarke, A. D. (1982) Effects of filter internal reflection coefficient on light absorption measurements made using the integrating plate method. Appl. Optics 21, 3021-3031.

Cunningham, P. T., S. A. Johnson, and R. R. Yang (1974) Variations in chemistry of airborne particulate material with particle size and time. Environ. Sci. Technol. 8, 131-135.

Daisey, J. M. (1980) Organic compounds in urban aerosols. Annals of the New York Academy of Sciences 338, 50-69.

Dangler, M., B. Steven, S. V. Hering, and D. T. Allen (1987) A direct FTIR method for identifying functional groups, in size segregated atmospheric aerosols. Atmos. Environ. 21, 1001-1004.

Friedel, R. A. and L. J. E. Hofer (1970) Spectral characterization of activated carbon. J. Phys. Chem. 74, 2921-2922.

Griffiths, P. R. and J. A. de Haseth (1986) Fourier Transform Infrared Spectroscopy, Wiley Interscience, New York, 339.

Grosjean, D. (1975) Solvent extraction and organic carbon determination in atmospheric particulate matter: the organic extraction-organic carbon analyzer (OE-OCA) technique. Anal. Chem. 47, 797-805.

Hansen, A. D. A., H. Rosen, and T. Novakov (1984) The aethalometer - an instrument for the real-time measurement of optical absorption by aerosol particles. The Sci. of the Tot. Environ. 36, 191-196.

Harrison, R. M. and W. T. Sturges (1984) Physico-chemical speciation and transformation reactions of particulate atmospheric nitrogen and sulphur compounds. Atmos. Environ. 18, 1829-1833.

Herzberg, G. (1964) Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York.

Hirschfeld, T. (1975a) Direct recording of intermolecular interaction perturbation spectra fourier transform spectroscopy. Appl. Spectrosc. 29, 345-351.

Hirschfeld, T. (1975b) Determination of wavelength scale repeatabilities in computerized spectrometers. Appl. Spectrosc. 29, 524-525.

Hirschfeld, T. (1976) Instrumental requirements for absorbance subtraction. Appl. Spectrosc. 30, 550-551.

Howes, J. E. (1987) Results of Carbon, Sulfate, Nitrate, Ammonium, and Mass Measurements Performed During the CARB Carbon Species Study. Environmen- tal Monitoring and Services, Inc. Report EMSI-1140.32FR, Camarillo, CA.

Huntzinger, J. J., R. L. Johnson, J. J. Shah, and R. A. Cary (1982) Analysis of organic and elemental carbon in a ambient aerosols by a thermal-optical method. In Particulate Carbon: Atmospheric Life Cycle (G. T. Wolff and R. L. Klimisch, eds.) Plenum Press, New York, 79-88.

Jaklevic J. M., D. A. Landis, and F. D. Goulding (1976) Energy dispersive x-ray fluorescence spectrometry using pulsed x-ray excitation. In Advances in X-ray Analysis (R. W. Gould, C. S. Barrett, J. B. Newkirk, and C. O. Rudd, eds.) Kendahl/Hunt, Dubuque, IA 19, 253-265.

Jennings, S. G., R. G. Pinnick, and H. J. Auverman (1978) Effects of particulate complex refractive index and particle size distribution variations on atmospheric extinction and absorption for visible through middle IR wavelengths. Appl. Optics 17, 3922-3929.

Johnson, S. A., R. Kumar, and P. T. Cunningham (1983) Airborne detection of acidic sulfate aerosol using an ATR impactor. Aerosol Sci. Technol. 2, 401-405.

Lin, C., M. Baker, and R. J. Charlson (1973) Absorption coefficient of atmospheric aerosol: a method for measurement. Appl. Optics 12, 1356-1363.

Long, G. L. and J. D. Winefordner (1983) Limit of detection, a closer look at the IUPAC definition. Anal. Chem. 55, 712-724A.

Loo, B. W., R. S. Adachi, C. P. Cork, F. S. Goulding, J. M. Jaklevic, D. A. Landis, and W. L. Searles (1979) A second generation dichotomous sampler for large-scale monitoring of airborne particulate matter. Lawrence Berkeley Laboratory Report LBL-8725.

Mattson, J. S. and H. B. Mark (1969) Infrared internal reflectance spectroscopic determination of surface functional groups on carbon. J. Colloidal and Interface Sci. 31, 131-144.

May, K. R. (1973) The collision nebulizer: description, performance, and application. Aerosol Sci. 4, 235-243.

McClenny, W. A., J. W. Childers, R. Rohl, and R. A. Palmer (1985) FTIR transmission spectrometry for the nondestructive determination of ammonium and sulfate in ambient aerosols collected on teflon filters. Atmos. Environ. 19, 1891-1898.

Mulik, J. D., R. Puchett, D. Williams, and E. Sawicki (1976) Ion chromatographic analysis of sulfate and nitrate in ambient aerosols. Anal. Lett. 9, 653-663.

Novakov, T. (1984) The role of soot and primary oxidants in atmospheric chemistry. The Sci. of the Tot. Environ. 36, 1-10.

Pilinis, C., J. H. Seinfeld, and C. Seigneur (1987) Mathematical modeling of the dynamics of multicomponent atmospheric aerosols. Atmos. Environ. 21, 943-955.

Pollard, M. J. and J. M. Jaklevic (1986) Fourier transform infrared spectroscopy (FTIR) ammonium sulfate analysis on teflon air filters. In Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants, 865-874.

Roessler, D. M. (1982) Diesel particle mass concentration by optical techniques. Appl. Optics 21, 4077-4086.

Rosen, H. and T. Novakov (1983) Optical transmission through aerosol deposits on diffusely reflective filters: a method for measuring the absorbing component of aerosol particles. Appl. Optics 22, 1265-1266.

Stelson, A. W. and J. H. Seinfeld (1982) Thermodynamic prediction of the water activity, NH_4NO_3 dissociation constant, density and refractive index for the NH_4NO_3-$(NH_4)_2SO_4$-H_2O system at 25°C. Atmos. Environ. 16, 2507-2514.

Stelson, A. W., S. K. Friendlander, and J. H. Seinfeld (1979) A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate. Atmos. Environ. 13, 369-371.

Stevens, R. K., T. G. Dzubay, G. Russwurm, and D. Rickel (1978) Sampling and analysis of atmospheric sulfates and related species. Atmos. Environ. 12, 55-68.

Tang, I. N., W. T. Wong, and H. R. Munkelwitz (1981) The relative importance of atmospheric sulfates and nitrates in visibility reduction. Atmos. Environ. 15, 2463-2753.

Tani, B., S. Siegel, S. A. Johnson, and R. Kumar (1983) X-ray diffraction investigation of atmospheric aerosols in the 0.3 - 1.0 μm aerodynamic size range. Atmos. Environ. 17, 2277-2283.

Van Vaeck, L. and K. Van Cauwenberghe (1978) Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric particulate matter. Atmos. Environ. 12, 2229-2239.